

CORRELATION AND PREDICTION OF VAPOUR-LIQUID EQUILIBRIUM THROUGH EQUATION OF STATE USING WONG SANDLER MIXING RULES

*A Thesis Submitted in Partial
Fulfilment of the Requirements
for the Degree of
Master of Technology*

by

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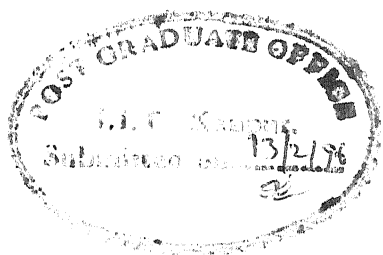
CERTIFICATE

It is certified that the work contained in the thesis titled **Correlation and prediction of vapour-liquid equilibrium through equation of state using Wong-Sandler mixing rules**, by *Sumanta Ghosh*, has been carried out under my supervision and that this work has not been submitted elsewhere for a degree.



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Abstract

It is well known that highly polar and hydrogen bonding mixtures pose a serious challenge to equations of state. In the present work, it has been shown that excellent correlation and predictions of the behaviour for complex systems can be achieved when Wong-Sandler mixing rules are associated with a proper equation of state. In the present work, vapour-liquid equilibrium (VLE) calculations have been carried out for 15 binary and 5 ternary systems and the systems are ~~so~~ chosen such that each system contains at least one polar substance. It is found that, Peng, Robinson, Stryjek and Vera (PRSV) equation of state along with Wong-Sandler mixing rules predicts VLE data which is in good agreement with experimental data. The Wong-Sandler mixing rules depend on two parameters, the excess molar Helmholtz free energy and second virial coefficient. The excess molar Helmholtz free energy is calculated by Nonrandom, Two-Liquid (NRTL) model and the cross second virial coefficient is calculated from Tsonopoulos correlation.

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SUMANTA GHOSH

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Nomenclature

| Symbols | Descriptions |
|------------------|--|
| A | Helmholtz free energy |
| a | Energy parameter in van der Waals equation |
| a^E | Excess molar Helmholtz free energy |
| B_{ij} | Second virial coefficient |
| B_{12}^{EOS} | Cross second virial coefficient from equation of state |
| B_{12}^{exp} | Cross second virial coefficient from experimental data |
| b | Excluded volume |
| C | Third virial coefficient |
| cT | Cross temperature |
| D | Parameter in Wong-Sandler mixing rules |
| f_i | Fugacity of i th component |
| G | Gibbs free energy |
| G_{ji} | NRTL parameter |
| g^E | Excess molar Gibbs free energy |
| g_{ii}, g_{ji} | NRTL parameter |
| H | Enthalpy |
| K_{ij} | Tsonopoulos binary interaction parameter |
| k_{ij} | Second virial coefficient binary interaction parameter |
| M_i | Molecular weight |
| n_i | Number of moles of i th component |
| P | Pressure |
| P_c | Critical pressure |
| p^{exp} | Experimental pressure |
| p^{cal} | Calculated pressure |
| Q | Parameter in Wong-Sandler mixing rules |
| R | Universal gas constant |
| S | Entropy |
| s | Molar entropy |

| Symbols | Descriptions |
|----------------------|---|
| T | Absolute temperature |
| T_c | Critical temperature |
| t^{exp} | Experimental temperature |
| t^{cal} | Calculated temperature |
| U | Internal energy |
| V | Total volume |
| v | Molar volume |
| \bar{v} | Partial molar volume |
| v_c | Critical molar volume |
| x_i | Liquid phase mole fraction of i th component |
| y_i | Vapour phase mole fraction of i th component |
| y_i^{exp} | Experimental vapour phase mole fraction of i th component |
| y_i^{cal} | Calculated vapour phase mole fraction of i th component |
| z | Compressibility factor |
| z_c | Critical compressibility factor |
| <u>Greek letters</u> | |
| α | A function of reduced temperature |
| α_{ij} | Nonrandomness parameter |
| μ | Dipole moment |
| μ_i | Chemical potential of i th component |
| ϕ_i | Fugacity coefficient of i th component |
| γ_i | Activity coefficient of i th component |
| ω | Acentric factor |
| σ | A constant, depends on equation of state |
| τ_{ji} | NRTL parameter |
| <u>Superscripts</u> | |
| V | Vapour phase |
| L | Liquid phase |
| o | At standard conditions |
| <u>Subscripts</u> | |
| c | Critical point |
| i, j, k, m | Components |
| r | Reduced condition |

Chapter 1

INTRODUCTION

In chemical and petroleum industries, the separation of components from a mixture is one of the important tasks. In the manufacture of chemical products, several operations like extraction, adsorption, distillation, leaching and absorption are associated with phase-contacting. For the design engineer whose interest lies in sizing the equipment, predicting the operating costs and designing control schemes for new and existing separation processes, a knowledge of the thermodynamic behaviour of the systems becomes invaluable.

Of all the separation processes, distillation is probably the most widely used in chemical industries, where the coexisting phases are vapour and liquid. Hence for the design of distillation columns, it is necessary to have reliable Vapour-Liquid Equilibrium (VLE) data. For a large number of binary and for a few multicomponent systems the experimental VLE data can be found in the literature. However the number of possible combinations of components of interest in chemical process design always far exceed the number of systems for which experimental VLE data are available. This necessitates the designer either to experimentally determine or theoretically estimate the required VLE data.

One of the most important tasks of a design engineer is to develop a mathematical model to predict the behaviour of the systems. Among the several techniques of phase equilibrium calculations the analytic combined methods (Gamma-Phi approach) and the analytic direct methods (Equation of state approach) are widely used. There are two classes of thermodynamic models for phase equilibrium calculations: equations of state and activity coefficient (free energy) models. The regions of applicability of these models are schematically illustrated in Figure 1.1, where the axes are density and complexity of the mixture represented by the excess free energy in a high density

state.

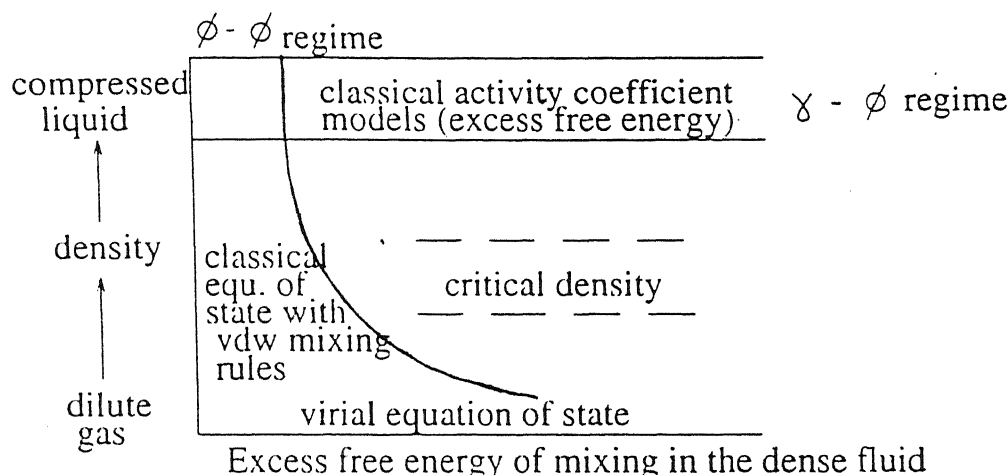


Figure 1.1, Schematic diagram of the approximate range of applicability of various thermodynamic models.

The virial equation of state can be used at low densities to describe any mixture provided all the virial coefficients are available. Activity coefficient models can also be used to describe the behaviour of liquid of any complexity, but only below its critical temperature. Cubic equations of state, with the usual Van der Waals one fluid mixing rules, can be used at all densities but only for relatively simple mixtures (i.e., hydrocarbons or hydrocarbons and inorganic gases) with low to moderate excess free energies.

Equations of state applicable to both vapour and liquid phases have obvious advantages over activity coefficient models, especially when one is interested in large ranges of temperature and pressure including critical and super critical regions. However, phase equilibrium calculations by this method are rather lengthy except for simple equations of state. Another problem with the use of the equations of state technique is the insufficiency of information about the exact form of equations of state for mixtures and inaccuracy of the existing mixing rules for mixtures consisting of polar and associated molecules of large molecular size and shape differences. Recently, Wong and Sandler (1992) have developed a new theoretically correct equation of state mixing model which is not only conceptually simple, but more accurate for wider ranges of mixtures than other existing mixing models.

In the present work, Wong and Sandler's mixing rule is clubbed with Peng, Robinson, Stryjek and Vera (PRSV) equation of state (or modified Peng-Robinson equation of state) to predict VLE data for few systems through $\phi - \phi$ approach. In Wong-Sandler mixing rule the excess molar Helmholtz free energy and the activity coefficients are calculated by Non Random Two Liquid (NRTL) model. The cross second virial coefficients B_{ij} are calculated by Tsonopoulos correlation (1974).

Chapter 2

THERMODYNAMICS OF PHASE EQUILIBRIUM

2.1 The General VLE Problems

In general, VLE problems are classified into four classes. They are,

BUBL P : Calculate y_k and P , given x_k and T

DEW P : Calculate x_k and P , given y_k and T

BUBL T : Calculate y_k and T , given x_k and P

DEW T : Calculate x_k and T , given y_k and P

Thus, for a system containing N components, one specifies either T or P and either the liquid phase or the vapour phase composition, fixing $1 + (N - 1)$ or N phase rule variables, which are the exact number required by the phase rule, for the specification of two coexisting vapour-liquid phases. The total number of variables, to be determined, are $N + 2$, which includes vapour and liquid volumes. Hence, one needs $N + 2$ equations, to solve these $N + 2$ variables. The required equations are as follows :

- (1) N equilibrium relationships for N components.
- (2) The equation of state for vapour phase.
- (3) The equation of state for liquid phase.

Since all the $(N + 2)$ variables are involved implicitly in these equations, one must employ iterative procedure to determine these variables.

2.2 Thermodynamic Relationships and Equations

The internal energy of a closed, homogeneous system can be expressed as

$$dU = TdS - PdV \quad (2.1)$$

Here U is the internal energy, S is the entropy, and V is the volume. For a system to be at equilibrium, the internal energy should reach a minimum value at constant S and V . That is

$$dU_{S,V} = 0 \quad (2.2)$$

The following expression can be used in the calculation of energy changes, if the enthalpy H , is defined as:

$$H = U + PV \quad (2.3)$$

From equations (2.1) and (2.3), one can get

$$dH = TdS + VdP \quad (2.4)$$

To use temperature explicit and volume explicit expressions in the calculation of energy the Helmholtz energy, A is defined as

$$A = U - TS \quad (2.5)$$

Differentiating and substituting equation (2.5) into equation (2.1) yields

$$dA = -SdT - PdV \quad (2.6)$$

Equation (2.1) can also be rearranged so that the calculation of energy is made using expressions explicit in temperature and pressure. The arrangement is as follows :

$$G = H - TS \quad (2.7)$$

Here G is the Gibbs free energy. Differentiation and substitution yields

$$dG = -SdT + VdP \quad (2.8)$$

For equilibrium at constant temperature and pressure the Gibbs free energy must be at a minimum. That is

$$dG_{T,P} = 0 \quad (2.9)$$

2.3 Chemical Potential

Equations (2.1), (2.4), (2.6), (2.8) are valid for systems containing only one component. For multicomponent systems, the internal energy is also a function of the number of moles of each component present.

$$U = U(S, V, n_1, n_2, \dots, n_m) \quad (2.10)$$

If we define chemical potential as

$$\mu_i = \left(\frac{\partial U}{\partial n_i} \right)_{S,V,n_j} = \left(\frac{\partial H}{\partial n_i} \right)_{S,P,n_j} = \left(\frac{\partial A}{\partial n_i} \right)_{T,V,n_j} = \left(\frac{\partial G}{\partial n_i} \right)_{T,P,n_j} \quad (2.11)$$

Substituting the definition of *chemical potential* equations (2.1), (2.4), (2.6), and (2.8) reduce to

$$dU = TdS - PdV + \sum_i \mu_i dn_i \quad (2.12)$$

$$dH = TdS + VdP + \sum_i \mu_i dn_i \quad (2.13)$$

$$dA = -SdT - PdV + \sum_i \mu_i dn_i \quad (2.14)$$

$$dG = -SdT + VdP + \sum_i \mu_i dn_i \quad (2.15)$$

To have a better understanding of the physical significance of the chemical potential, one can inspect the terms of equation (2.12). If one considers the temperature as a measure of thermal driving force and pressure as a mechanical driving force, then the use of the term *chemical potential* makes more sense. When a closed, heterogeneous system is at equilibrium, these potentials, or intensive properties, are equal for each component in each phase. If a system of m components has vapour and liquid phases in equilibrium, the following relationships hold :

$$T^V = T^L \quad (2.16)$$

$$P^V = P^L \quad (2.17)$$

$$\mu_1^V = \mu_1^L \quad (2.18)$$

$$\mu_2^V = \mu_2^L$$

$$\vdots \quad \vdots$$

$$\mu_m^V = \mu_m^L$$

2.4 Fugacity and Fugacity Coefficient

The practical convenience dictates that the thermodynamic relationships for a system must be in terms of experimentally measurable quantities. In the case of phase equilibrium, the temperature and pressure can be directly measured, where as the chemical potential can not be. To overcome this difficulty, one must express the

chemical potential in terms of experimentally measurable quantities. By differentiating equation (2.7) and combining the result with the first and second laws of thermodynamics the following equations can be derived.

$$d\mu_i = -s_i dT + v_i dP \quad (2.19)$$

and

$$\left(\frac{\partial \mu_i}{\partial P} \right)_T = v_i \quad (2.20)$$

Here s_i is the molar entropy and v_i is the molar volume.

In the case of ideal gas,

$$v_i = \frac{RT}{P} \quad (2.21)$$

Substituting equation (2.21) in equation (2.20) and integrating at constant temperature yields

$$\mu_i - \mu_i^0 = RT \ln \frac{P}{P^0} \quad (2.22)$$

where the superscript 0 signifies a reference state for the quantity. Although we do not have a direct means of calculating the chemical potential we do have an expression for the change in the chemical potential of an ideal gas as the pressure changes from some reference pressure P^0 to the pressure P . Equation (2.22) relates the chemical potential to the experimental quantities — pressure and temperature.

Unfortunately, equation (2.22) is valid only for an ideal gas. To extend the relationship to nonideal gases, *G. N. Lewis* defined a function f , called the fugacity, by the relation

$$\mu_i - \mu_i^0 = RT \ln \frac{f_i}{f_i^0} \quad (2.23)$$

For ideal gases, the fugacity is equal to the pressure, and for mixtures of ideal gases, the fugacity of a component is equal to its partial pressure. The fugacity is often referred to as a *corrected pressure*. If one considers two phases α and β in equilibrium and sets

$$\mu_i^{0\alpha} = \mu_i^{0\beta} \quad (2.24)$$

it follows that

$$f_i^{0\alpha} = f_i^{0\beta} \quad (2.25)$$

and

$$f_i^\alpha = f_i^\beta \quad (2.26)$$

The fugacity coefficient of a component i , ϕ_i is defined as

$$\phi_i = \frac{f_i}{y_i P} \quad (2.27)$$

^{at low pressure}
In an ideal solution the fugacity coefficient of a component is equal to unity. The greater the fugacity coefficient deviates from unity, the greater the system deviates from ideal solution behaviour.

2.5 Equation of State Approach

Starting with the definitions of enthalpy, entropy, Helmholtz energy and Gibbs free energy, we can arrive at the following relationship for the fugacity of component i in a mixture :

$$RT \ln \phi_i = RT \ln \frac{f_i}{y_i P} = \int_0^P \left[\tilde{v}_i - \frac{RT}{P} \right] dP \quad (2.28)$$

Here, \tilde{v}_i is the partial molar volume of i which is defined as

$$\tilde{v}_i = \left(\frac{\partial V}{\partial n_i} \right)_{T, P, n_j} \quad (2.29)$$

For pure components, the partial molar volume \tilde{v}_i is equal to the molar volume v_i , and equation (2.28) reduces to

$$RT \ln \frac{f}{P} = \int_0^P \left[v_i - \frac{RT}{P} \right] dP \quad (2.30)$$

Unfortunately, explicit representation of volume by an equation of state is often difficult. A better alternative is to characterize the system with an equation of state explicit in pressure. For a given volume and temperature, the system can exist at only one pressure. In contrast, volume is not a unique function of temperature, pressure and concentration. For a pressure explicit equation of state, equation (2.28) can be written as

$$RT \ln \phi_i = RT \ln \frac{f_i}{y_i P} = \int_V^\infty \left[\left(\frac{\partial P}{\partial n_i} \right)_{T, V, n_j} - \frac{RT}{V} \right] dV - RT \ln z \quad (2.31)$$

Here z is the compressibility factor defined as $z = \frac{Pv}{RT}$

Equation (2.26) requires that for vapour-liquid equilibrium the fugacity of a component in the vapour phase is equal to the fugacity of that component in liquid phase. Substituting the definition of the fugacity coefficient in equation (2.26), one gets

$$y_i P \phi_i^V = x_i P \phi_i^L \quad (2.32)$$

$$\text{or} \quad y_i \phi_i^V = x_i \phi_i^L \quad (2.33)$$

Here, y_i is the mole fraction of component i in the vapour phase and x_i is the mole fraction of component i in the liquid phase.

In some cases the constants in the equation of state can be calculated solely from information about pure components constituting the system. Thus, these equations are predictive. Often the accuracy of the equation of state can be greatly enhanced by the introduction of some adjustable parameters, the values of which depend on the conditions of the system. With the introduction of adjustable parameters, the equation of state becomes a correlative method as opposed to a predictive one. Information about the system at discrete values of T , P and concentration is used to find optimum adjustable parameters, which in turn can be used for interpolation or extrapolation.

Chapter 3

EQUATIONS OF STATE AND MIXING RULES

By equations of state we refer to volumetric equations of state, that is, relationships between the pressure P , molar volume v , and absolute temperature T . From such a volumetric equation of state we get not only $P - v - T$ information but, also (from the interrelationships provided by classical thermodynamics) departure functions and phase equilibrium data. Despite the abundance of such equations of state, none has proven completely satisfactory for all areas of interest in scientific and engineering applications.

3.1 Ideal Gas Equation

The simplest volumetric equation of state for a gas, consistent with Boyle's law and Charles' law, is the ideal gas equation which is given by

$$Pv = RT \quad (3.1)$$

$$\text{or} \quad z = \frac{Pv}{RT} = 1 \quad (3.2)$$

where R is the universal gas constant and z is the compressibility factor. While this equation of state is satisfactory for nonassociating gases at low pressures, it does not give an adequate description of the behaviour of gases at moderate and high pressures, and it does not predict the occurrence of a vapour-liquid phase transition.

3.2 Cubic Equations of State

For an accurate description of the $P - v - T$ behaviour of fluids over wide ranges of temperature and pressure, an equation of state which is more comprehensive than the virial equation of state is required. Such an equation must be sufficiently general to apply to liquids as well as to gases and vapours. It must not be so complex as to present excessive numerical or analytical difficulties in applications. Polynomial equations that are cubic in molar volume offer a simplicity, which are in fact the simplest equations capable of representing both liquid and vapour phases.

But the simple equations are not accurate enough for the many $P - v - T$ representations, and a more complex form of equation such as *Benedict-Webb-Rubin* equation of state or *Beattie-Bridgeman* equation of state (which are having eight and five adjustable parameters respectively) is required to describe accurately the $P - v - T$ behaviour of real fluids. However, simple equations of state have found extremely valuable applications in phase equilibrium predictions, as demonstrated by *Soave* (1972), *Peng and Robinson* (1976) and *Benmékki and Mansoori* (1987) etc.

3.2.1 Van der Waals Equation of State

The first equation of state to give a qualitative description of the vapour and liquid phases and phase transitions was the famous cubic equation of *Van der Waals* (vdw), proposed in 1873.

$$P = \frac{RT}{(v - b)} - \frac{a}{v^2} \quad (3.3)$$

In this equation the constant b is the excluded volume, that is, that part of the molar volume which is not available to a molecule due to the presence of others. This contribution increases the pressure above that for an ideal gas at the same density and temperature. The second term on the right, which *Van der Waals* took to be independent of temperature, is due to attractive forces and decreases the pressure.

Van der Waals observed that the critical isotherm had a horizontal slope and an inflection point at the critical point, and utilized these characteristics in determining the parameters. Mathematically the conditions are expressed as

$$\left(\frac{\partial P}{\partial v} \right)_{T_c} = 0 \quad (3.4)$$

$$\left(\frac{\partial^2 P}{\partial^2 v} \right)_{T_c} = 0 \quad (3.5)$$

Then by applying these conditions to equation (3.3) one can get

$$b = \frac{RT_c}{8P_c} \quad (3.6)$$

$$a = (27/64) R^2 T_c^2 / P_c \quad (3.7)$$

While *Van der Waals* equation of state is of historical interest, it is not quantitatively accurate. For example, it predicts that the critical compressibility,

$$z_c = \frac{P_c v_c}{RT_c} \quad (3.8)$$

is 0.375 for all fluids, while the value for different hydrocarbons varies from 0.24 to 0.29; the range is wider when nonhydrocarbons are considered. Also, the predicted vapour pressures by *Van der Waals* equation of state are inaccurate.

3.2.2 Redlich-Kwong (RK) Equation of State

An important modification of the *Van der Waals* equation of state was made by *Redlich* and *Kwong* (1949), who introduced a temperature dependent term and a slightly different volume dependence in the attractive term. The RK equation of state is given by

$$P = \frac{RT}{(v - b)} - \frac{a/T^{0.5}}{[v(v + b)]} \quad (3.9)$$

It is belived to be the first simple equation of state that found successful industrial applications. The improvement was so remarkable that many investigators have since attempted to make further improvement in the equation of state with varying degrees of success. This equation gives a somewhat better critical compressibility ($z_c = 1/3$), and better second virial coefficients (*Tsonopoulos* and *Heidman*, 1985) than the *Van der Waals* equation, but it is still not very accurate for the phase boundary (vapour pressure) and liquid density.

3.2.3 Soave-Redlich-Kwong (SRK) Equation of State

Wilson (1964) changed the temperature dependence of the attractive parameter in *Redlich-Kwong* equation by writing

$$P = \frac{RT}{v - b} - \frac{a(T)}{v(v + b)} \quad (3.10)$$

$$\text{where,} \quad a(T) = a(T_c) \cdot \alpha(T_r, \omega) \quad (3.11)$$

$$a(T_c) = 0.42747 \frac{R^2 T_c^2}{P_c} \quad (3.12)$$

$$b = 0.08664 \frac{RT_c}{P_c} \quad (3.13)$$

$$\alpha = T_r \left[1 + (1.57 + 1.62\omega) \left(\frac{1}{T_r} - 1 \right) \right] \quad (3.14)$$

where ω is the acentric factor (*Pitzer*, 1955, 1977) defined as

$$\omega = -\log \frac{P(T_r = 0.7)}{P_c} - 1.0 \quad \text{and} \quad T_r = \frac{T}{T_c} \quad (3.15)$$

However, it was *Soave's* modification (1972) for the α parameter,

$$\alpha = [1 + (0.48 + 1.57\omega - 0.176\omega^2)(1 - T_r^{0.5})]^2 \quad (3.16)$$

resulting in accurate vapour pressure predictions (especially above 1 bar) for light hydrocarbons, which led to cubic equations of state becoming an important tool for the prediction of vapour-liquid equilibria at moderate and high pressures for nonpolar fluids. This modification is referred to as the *Soave-Redlich-Kwong* or *SRK* equation.

3.2.4 Peng-Robinson (PR) Equation of State

There are some shortcomings which the *Soave-Redlich-Kwong* equation and the original *Redlich-Kwong* equation have in common. The most evident is the failure to generate satisfactory density values for the liquid even though the calculated vapour densities are generally acceptable. The other shortcoming is the prediction of an unrealistic universal critical compressibility factor of 1/3 for all substances. To alleviate these shortcomings, *Peng* and *Robinson* (1976) used a different volume dependence to give slightly improved liquid volumes (i.e., $z_c = 0.307$) and changed the temperature dependence of α to give more accurate vapour pressure prediction for hydrocarbons in the 6- to 10- carbon number range (i.e., gasoline fractions) as follows :

$$P = \frac{RT}{v - b} - \frac{a_c \alpha}{v(v + b) + b(v - b)} \quad (3.17)$$

with

$$\alpha = [1 + (0.37464 + 1.54226\omega - 0.26992\omega^2)(1 - T_r^{0.5})]^2 \quad (3.18)$$

$$a_c = 0.45724 \frac{R^2 T_c^2}{P_c} \quad (3.19)$$

$$b = 0.07780 \frac{RT_c}{P_c} \quad (3.20)$$

3.2.5 Peng-Robinson-Stryjek-Vera (PRSV) Equation of State

Although in many respects the modifications introduced in the modified *Peng-Robinson* (PRSV) equation of state by *Stryjek* and *Vera* (1986) follow ideas of previous workers in the field. The differences in the details are significant enough to produce a definite improvement with respect to other versions of cubic equations of state. In this equation all other parameters are the same as the *Peng-Robinson* equation of state except for α . The parameter α is given by

$$\alpha = [1 + k(1 - T_r^{0.5})]^2 \quad (3.21)$$

where k is considered to be a function of acentric factor ω only. After a careful examination of the deviations in the calculated vapour pressures at low reduced temperatures for compounds with a wide range of acentric factors, they have modified the functional dependence of k as

$$k = k_0 + k_1(1 + T_r^{0.5})(0.7 - T_r) \quad (3.22)$$

with

$$k_0 = 0.378893 + 1.4897153\omega - 0.17131848\omega^2 + 0.0196554\omega^3 \quad (3.23)$$

and k_1 , being an adjustable parameter characteristic of each pure substance.

The *Peng-Robinson* (PR) and SRK equations are widely used in industry, especially for refinery and reservoir simulation. The advantages of these equations are that they require little input information (only the critical properties and acentric factor for the generalized parameters), little computer time, and, for hydrocarbons, lead to good phase equilibrium predictions which is important for process design. However, these equations do have some important shortcomings. For example, liquid densities are not well predicted, the generalized parameters are not accurate for nonhydrocarbons (especially polar and associating fluids), and these equations do not lead to accurate predictions for long chain molecules. Also these equations are not accurate in the critical region, and vapour pressure predictions are not very accurate below 10 Torr. Even so, the *Soave* and *Peng-Robinson* equations are the most widely used cubic equations of state in industry.

3.3 Virial Equation of State

All the foregoing equations of state are empirical or at best semi- theoretical, but they are in closed form, which is of great advantage for practical applications. In contrast to the equations of state mentioned earlier, the virial equation of state has a theoretical basis from *statistical mechanics*, but has the form of an infinite power

series in volume, which is not convenient for practical use. The virial equation of state is given by

$$P = RT \left(\frac{1}{v} + \frac{B}{v^2} + \frac{C}{v^3} + \dots \right) \quad (3.24)$$

The virial coefficients B, C, D etc. are dependent only on temperature. This equation truncated after the second or third term depending on the availability of the virial coefficients is occasionally used for vapour phase properties calculations. Although, not widely used for predicting the phase equilibrium data, this equation is worth reviewing, because all the foregoing equations bear a formal resemblance to it when expanded into infinite series. For instance, if *Van der Waals* equation of state is expanded into infinite series, we get

$$P = \frac{RT}{v-b} - \frac{a}{v^2} = RT \left(\frac{1}{v} + \frac{b - \frac{a}{RT}}{v^2} + \frac{b^2}{v^3} + \dots \right) \quad (3.25)$$

All other closed forms of equations of state can be similarly expanded. The virial equation, originally suggested by *Onnes* as early as 1901, can be derived by the method of *statistical mechanics*. These methods show that the virial coefficients are precisely related to the molecular interactions of particular number of molecules. For instance, the second virial coefficient reflects the binary interactions and the third virial coefficient reflects the triple interactions and so on.

3.4 Mixing Rules for Cubic Equations of State

The equations of state are generally developed for pure fluids first, then extended to mixtures. The extension requires the so called mixing rules, which are simply means of calculating mixture parameters equivalent to those of pure substances. So far no exact theory like that for the virial equation prescribes this composition dependence, and quite often one relies on empirical mixing rules to provide approximate relationships. Recently *Wong* and *Sandler* (1992) have developed a new theoretically correct equation of state mixing model which is more accurate for a wider range of mixtures than other mixing models available.

3.4.1 Van der Waals Mixing Rules

The conventional *Van der Waals* type mixing rules are given by

$$a_m = \sum_i \sum_j x_i x_j a_{ij} \quad (3.26)$$

$$\text{and} \quad b_m = \sum_i \sum_j x_i x_j b_{ij} \quad (3.27)$$

$$a_{ij} = \sqrt{a_i a_j} (1 - k_{ij}) \quad (3.28)$$

$$b_{ij} = \frac{b_i + b_j}{2} (1 - h_{ij}) \quad (3.29)$$

where $k_{ij} = k_{ji}$ and $h_{ij} = h_{ji}$ are binary interaction parameters to be determined from the experimental vapour-liquid equilibrium data.

3.4.2 Linear Mixing Rules

The *linear* mixing rules are given by

$$a_m = \sum_i \sum_j x_i x_j a_{ij} ; \quad a_{ij} = \sqrt{a_i a_j} \quad (3.30)$$

$$\text{and} \quad b_m = \sum_i x_i b_i \quad (3.31)$$

3.4.3 Cubic Mixing Rules

The *cubic* mixing rules are given by

$$a_m^{1/3} = \frac{x_1(a_{11}M_1)^{1/3} + x_2(a_{22}M_2)^{1/3}}{x_1M_1^{1/3} + x_2M_2^{1/3}} + [(a_{11}a_{22})^{1/2}]^{1/3}x_1x_2(1 - k_{12}) \quad (3.32)$$

$$\text{and} \quad b_m = \sum_{i=1}^2 \sum_{j=1}^2 x_i x_j b_{ij} \quad (3.33)$$

$$\text{where,} \quad b_{ij} = \frac{b_i + b_j}{2} (1 - h_{ij}) \quad (3.34)$$

k_{ij} and h_{ij} are binary interaction parameters to be determined from experimental data. M_1, M_2 are molecular weights.

3.4.4 Wong-Sandler Mixing Rules

The *Wong-Sandler* mixing rules have been described in detail in chapter-4.

Chapter 4

WONG-SANDLER MIXING RULES FOR PRSV EQUATION OF STATE

While simple cubic equations of state can describe the behaviour of pure fluids reasonably well, they give satisfactory descriptions only for relatively simple mixtures. It has long been recognized that the source of this difficulty is the mixing and combining rules which are used to obtain the equation of state mixture parameters from the pure fluid parameters. Consequently, much effort in recent years has been devoted towards developing alternate mixing rules.

Several authors (*Panagiotopoulos and Reid, 1986; Adachi and Sugie, 1986; Sandoval et al., 1989; Schwartzenuber et al., 1989*) have proposed various modified forms of the *Van der Waals* mixing rules that use composition-dependent binary interaction parameters. For some highly non-ideal mixtures these rules have been used successfully. However, they are not generally applicable because in the low density limit they are inconsistent with the statistical mechanical result that the second virial coefficient must be a quadratic function of composition. Further, these rules may fail for simple mixtures (*Shibata and Sandler, 1988*).

To overcome these difficulties attempts have been made to develop density-dependent mixing rules (for example, *Luedecke and Prausnitz, 1985; Panagiotopoulos and Reid, 1986*) so that the correct low-density limit is recovered. Such an approach, however, is adhoc and does not preserve the cubic nature of equation of state when used for mixtures. There have been ongoing efforts to correct such deficiencies (*Schwartzenuber and Renon, 1991; Mathias et al., 1991*), but with little success.

An alternate approach for developing mixing rules was first proposed by *Huron and Vidal (1979)*. This method involves equating the excess Gibbs free energy at infinite pressure calculated from an equation of state to that calculated from the excess Gibbs free energy (activity coefficient) models for liquids. In order that the

excess Gibbs free energy at infinite pressure computed from an equation of state be finite, *Huron* and *Vidal* had equated the excess volume at infinite pressure to zero; otherwise, the Pv^E term becomes infinite. Consequently, a linear mixing rule for the excluded volume parameter b_m had to be used. It was pointed out by *Sheng et al.* (1992) that such an assumption is not necessary if one equates *excess Helmholtz free energy* instead of *excess Gibbs free energy*.

The *Huron* and *Vidal* mixing rule does not satisfy the requirement that the second virial coefficient is a quadratic function of composition, and therefore, is inconsistent with statistical mechanical theory. *Wong, Orbey* and *Sandler* (1992) have shown from experimental data that

$$g^E(T, P=1 \text{ bar}, x) = a^E(T, P=1 \text{ bar}, x) = a^E(T, P=\text{high pressure})$$

This provides the justification for using exactly same functional form for a^E at infinite pressure as has been used for g^E at low pressures. Further, it also explains why in *Wong Sandler's* mixing rule model parameters obtained from low pressures data can be used, without change, at high pressures in a^E . Consequently, this new class of mixing rules provide results that are correct at both the low density and high density limits without being density dependent. Moreover, these mixing rules show the correct quadratic composition dependence of the second virial coefficient.

4.1 The Mixing Model

It is important to accurately estimate the pure component vapour pressures for predicting the vapour-liquid equilibrium data with accuracy. Many of the components considered in this work do not fit the generalized correlation for the equation of state parameters of *Peng* and *Robinson*. Therefore, the present work considers the correlation of *Stryjek* and *Vera* (1986) which is given below.

$$P = \frac{RT}{v-b} - \frac{a}{v(v+b) + b(v-b)} \quad (4.1)$$

In this equation of state, P , T , v and R are the pressure, temperature, molar volume and universal gas constant respectively. The parameters a and b are given by

$$a = (0.457235 R^2 T_c^2 / P_c) \alpha(T) \quad (4.2)$$

$$b = 0.077796 RT_c / P_c \quad (4.3)$$

$$\alpha(T) = [1 + k(1 - T_r^{0.5})]^2 \quad (4.4)$$

$$k = k_0 + k_1(1 + T_r^{0.5})(0.7 - T_r) \quad (4.5)$$

$$\text{and } k_0 = 0.378893 + 1.4897153\omega - 0.17131848\omega^2 + 0.0196554\omega^3 \quad (4.6)$$

where ω is the acentric factor, T_c is the critical temperature, P_c is the critical pressure, $T_r = T/T_c$, and k_1 is a constant specific to each fluid.

If we expand *PRSV* equation of state as a virial series, the relation between the second virial coefficient $B(T)$ and the equation of state parameters is given by

$$B(T) = b - \frac{a}{RT} \quad (4.7)$$

From *Statistical mechanics*, the composition dependence of the second virial coefficient can be expressed as

$$B_m(T) = \sum_i \sum_j x_i x_j B_{ij}(T) \quad (4.8)$$

Therefore,

$$b_m - \frac{a_m}{RT} = \sum_i \sum_j x_i x_j \left(b - \frac{a}{RT} \right)_{ij} \quad (4.9)$$

where $[b - a/(RT)]_{ij}$ is the composition independent cross second virial coefficient of the equation of state. A sufficient but not necessary, condition for satisfying equation (4.9) is the *Van der Waals* one fluid model. Traditionally this solution has been used at all densities.

Huron and *Vidal* (1979) developed a mixing rule by requiring that the excess Gibbs free energy (g^E) at infinite pressure (or $v = b$) computed from an equation of state be equal to that computed from an activity coefficient model resulting in

$$a = b \left[\sum_i x_i (a_i/b_i) - \sigma g^E \right] \quad (4.10)$$

where σ is a numerical constant which depends on the particular equation of state used. While this model, and its variations, have been successfully used for some complex mixtures, it is no better than the *Van der Waals* one fluid mixing rule for hydrocarbon systems. Further, *Huron* and *Vidal* mixing rules suffer from the drawback that they do not satisfy the second virial coefficient boundary condition.

Recently *Wong* and *Sandler* (1992) have shown that it is possible to satisfy the second virial coefficient boundary condition. Moreover they have also shown that the equation of state predicts the same excess Helmholtz free energy at infinite pressure a_∞^E as a function of composition as is obtained from an activity coefficient model with the following mixing model :

$$b_m = \frac{\sum_i \sum_j x_i x_j \left(b - \frac{a}{RT} \right)_{ij}}{1 + \frac{a_\infty^E(x)}{RT} - \sum_i x_i \left(\frac{a_i}{b_i RT} \right)} \quad (4.11)$$

and

$$a_m = b_m \left[\sum_i x_i \frac{a_i}{b_i} - \frac{a_\infty^E(x)}{\sigma} \right] \quad (4.12)$$

where σ , depends on the equation of state used. The value of σ is equal to $[\ln(2^{0.5} - 1)]/2^{0.5}$ for *PRSV* equation of state. The cross second virial coefficient is given by

$$\left(b - \frac{a}{RT}\right)_{ij} = \frac{\left(b_i - \frac{a_i}{RT}\right) + \left(b_j - \frac{a_j}{RT}\right)}{2}(1 - k_{ij}) \quad (4.13)$$

where k_{ij} is now a binary interaction parameter for the second virial coefficient. *Wong, Orbey and Sandler* (1992) have shown that for highly nonideal mixtures, once this second virial coefficient binary interaction parameters are obtained at a single temperature or pressure, the results can be extrapolated with very good accuracy over a range of 200⁰ C in temperature and hundreds of bars in pressure.

4.2 Second Virial Coefficient Binary Interaction Parameter

Eubank, Shyu and Hanif (1995) have studied in detail the *P-v-T* behaviour of different polar and nonpolar systems and they have observed that for nonpolar systems B_{ii}^{EOS} is not greatly different from B_{ii}^{exp} , whereas for polar systems B_{ii}^{EOS} is greatly different from B_{ii}^{exp} . They then realized that the approximation

$$B_{12}^{EOS} \simeq B_{12}^{exp} \quad (4.14)$$

is satisfactory even when B_{ii}^{EOS} differs significantly from B_{ii}^{exp} . Further, from experimental study of various systems they have seen that B_{12}^{EOS} equals to B_{12}^{exp} near $T_{r,12}$ of 0.84 ± 0.04 , where

$$T_{r,12} = \frac{T}{T_{c,12}} \quad (4.15)$$

$$T_{c,12} = \sqrt{T_{c1}T_{c2}(1 - K_{12})} \quad (4.16)$$

One can choose the value of this K_{12} as prescribed by *Tsonopoulos*, 1974 and *Tsonopoulos*, 1979 or one can tune this value in order to match with experimental VLE data.

In the present work, B_{12}^{exp} has been calculated by *Tsonopoulos correlation*. *Tsonopoulos* correlation for B_{12} in the case of nonpolar molecules is given by

$$\frac{B_{12}P_{c,12}}{RT_{c,12}} = B_{12}^{(0)} + \omega_{12}B_{12}^{(1)} \quad (4.17)$$

and for polar molecules it is given by

$$\frac{B_{12}P_{c,12}}{RT_{c,12}} = B_{12}^{(0)} + \omega_{12}B_{12}^{(1)} + B_{12}^{(2)} \quad (4.18)$$

where,

$$B_{12}^{(0)} = 0.1445 - \frac{0.330}{T_{r,12}} - \frac{0.1385}{T_{r,12}^2} - \frac{0.0121}{T_{r,12}^3} - \frac{0.000607}{T_{r,12}^8} \quad (4.19)$$

$$B_{12}^{(1)} = 0.0637 + \frac{0.331}{T_{r,12}^2} - \frac{0.423}{T_{r,12}^3} - \frac{0.008}{T_{r,12}^8} \quad (4.20)$$

$$\text{and} \quad B_{12}^{(2)} = \frac{a_{12}}{T_{r,12}^6} - \frac{b_{12}}{T_{r,12}^8}$$

Neither a nor b can be estimated with much accuracy. *Tsonopoulos*, however has correlated a and b for several compound classes. b is zero for nonhydrogen bonded materials, and a is given by the values or expressions. These expressions are functions of reduced dipole moment, which is defined as

$$\mu_r = \frac{10^5 \mu^2 P_c}{T_c^2} \quad (4.21)$$

where,

μ = dipole moment, debyes

P_c = critical pressure, bars

T_c = critical temperature, K

Mixing rules for critical properties as prescribed by *Tsonopoulos* (1974) are as given below.

$$T_{cij} = \sqrt{T_{ci} T_{cj}} (1 - K_{ij}) \quad (4.22)$$

$$P_{cij} = \frac{4T_{cij}(P_{ci}v_{ci}/T_{ci} + P_{cj}v_{cj}/T_{cj})}{(v_{ci}^{1/3} + v_{cj}^{1/3})^3} \quad (4.23)$$

$$\omega_{ij} = \frac{\omega_i + \omega_j}{2} \quad (4.24)$$

The following steps can be adopted to calculate the second virial coefficient binary interaction parameter.

- (1) Set $T_{r,12}$ equal to 0.84 ± 0.04 .
- (2) Calculate $T_{c,12}$, $P_{c,12}$ and ω_{12} by *Tsonopoulos* mixing rules.
- (3) Find cross temperature, $cT = T_{r,12} * T_{c,12}$
- (4) Find B_{11}^{EOS} and B_{22}^{EOS} from equation of state at this cross temperature. Calculate B_{12}^{exp} by *Tsonopoulos correlation* at this cross temperature. Since, for almost all systems this cross temperature is very high, the polar contribution in *Tsonopoulos correlation* (i.e., $B^{(2)}$) at this high temperature is negligible. This means that at higher temperatures polar molecules behave like nonpolar molecules. So, for correlation of B_{12}^{exp} we can use successfully *Tsonopoulos correlation* of nonpolar molecules for both polar and nonpolar molecules.
- (5) $B_{12}^{EOS} = B_{12}^{exp}$
- (6) Calculate second virial coefficient binary interaction parameters as

$$k_{12} = 1 - [2B_{12}^{EOS} / (B_{11}^{EOS} + B_{22}^{EOS})] \quad (4.25)$$

This k_{12} can be used by extrapolating with very good accuracy over 200° C in temperature and 100 bar in pressure.

4.3 Liquid and Vapour Volumes

The *PRSV* equation of state can be rewritten as,

$$z^3 + (B - 1)z^2 + (A - 3B^2 - 2B)z + (B^2 + B^3 - AB) = 0 \quad (4.26)$$

where,

$$A = \frac{aP}{R^2T^2} \quad (4.27)$$

$$B = \frac{bP}{RT} \quad (4.28)$$

$$z = \frac{Pv}{RT} \quad (4.29)$$

The first step in the application of these equations is the calculation of liquid and vapour densities which satisfy the above equation for a given temperature, pressure and sets of vapour and liquid compositions.

This cubic equation in z has either three real roots or one real root and two conjugate imaginary roots (*Sokolnikoff*, 1941). For the case where three real roots exist, the smallest root corresponds to the liquid phase and is called the liquid root and the largest root corresponds to the vapour phase and is called the vapour root. The intermediate root has no physical meaning. As far as the mixtures are concerned, liquid root has been taken while solving for liquid phase and vapour root has been taken while solving for vapour phase. In case of one real root, it has been used as liquid root for liquid phase and as vapour root for vapour phase. *Newton - Raphson* iterative procedure has been used for solving the cubic equation. Iteration can be started from $z = 0$ for liquid phase and from $z = 1$ for vapour phase.

4.4 Nonrandom, Two-Liquid (NRTL) Method

The concept of local composition has been successfully used by *Renon* in his derivation of the *nonrandom, two-liquid (NRTL)* equation. However *Renon's* equation, unlike *Wilson's*, is applicable to partially miscible as well as completely miscible systems. For a solution of m components, the *NRTL* equation for the excess Gibbs free energy is given by

$$\frac{g^E}{RT} = \sum_{i=1}^m x_i \frac{\sum_{j=1}^m \tau_{ji} G_{ji} x_j}{\sum_{l=1}^m G_{li} x_l} \quad (4.30)$$

where,

$$\tau_{ji} = \frac{g_{ji} - g_{ii}}{RT} \quad (4.31)$$

$$G_{ji} = \exp(-\alpha_{ji}\tau_{ji}) \quad (\alpha_{ji} = \alpha_{ij}) \quad (4.32)$$

The activity coefficient for a component i is given by

$$\ln \gamma_i = \frac{\sum_{j=1}^m \tau_{ji} G_{ji} x_j}{\sum_{l=1}^m G_{li} x_l} + \sum_{j=1}^m \frac{x_j G_{ij}}{\sum_{l=1}^m G_{lj} x_l} \left(\tau_{ij} - \frac{\sum_{r=1}^m x_r \tau_{rj} G_{rj}}{\sum_{l=1}^m G_{lj} x_l} \right) \quad (4.33)$$

g_{ij} is an energy parameter characteristic of the i - j interaction. The parameter α_{ij} is related to the nonrandomness in the mixture. When α_{ij} is zero the mixture is completely random and equation (4.30) reduces to the two suffix *Margules* equation. For moderately nonideal systems, the *NRTL* equation offers no advantages over the simpler *van Laar* and three suffix *Margules* equations. However for strongly nonideal mixtures, and especially for partially immiscible systems, the *NRTL* equation often provides a good representation of experimental data provided care is exercised in data reduction to obtain the adjustable parameters.

4.5 Other Necessary Expressions For VLE Calculation

The parameter σ , appearing in equation (4.10) is a numerical constant which depends on the particular equation of state used. The value of σ for *PRSV* equation of state is given by

$$\sigma = \frac{1}{\sqrt{2}} \ln(\sqrt{2} - 1) \quad (4.34)$$

The excess molar Helmholtz free energy at infinite pressure is given by

$$\frac{a_\infty^E}{\sigma RT} = \frac{a_m}{b_m RT} - \sum_i x_i \frac{a_i}{b_i RT} \quad (4.35)$$

The above expression can be split into the following two equations

$$b_m = \frac{Q}{(1-D)} \quad (4.36)$$

$$a_m = Q \frac{D}{(1-D)} \quad (4.37)$$

with Q and D defined as :

$$Q = \sum_i \sum_j x_i x_j \left(b - \frac{a}{RT} \right)_{ij} \quad (4.38)$$

$$D = \sum_i x_i \frac{a_i}{b_i RT} + \frac{a_\infty^E}{\sigma RT} \quad (4.39)$$

When *PRSV* equation of state is used, equation (2.31) reduces to

$$\ln \phi_i = -\ln \left[\frac{P(v - b_m)}{RT} \right] + \frac{1}{b_m} \left(\frac{\partial n b_m}{\partial n_i} \right) \left(\frac{Pv}{RT} - 1 \right) + \frac{1}{2\sqrt{2}} \left(\frac{a_m}{b_m RT} \right) \left[\frac{1}{a_m} \left(\frac{1}{n} \frac{\partial n^2 a_m}{\partial n_i} \right) - \frac{1}{b_m} \left(\frac{\partial n b_m}{\partial n_i} \right) \right] \ln \left[\frac{v + b_m(1 - \sqrt{2})}{v + b_m(1 + \sqrt{2})} \right] \quad (4.40)$$

The partial derivatives of a_m and b_m are given by

$$\frac{\partial n b_m}{\partial n_i} = \frac{1}{(1 - D)} \left(\frac{1}{n} \frac{\partial n^2 Q}{\partial n_i} \right) - \frac{Q}{(1 - D)^2} \left(1 - \frac{\partial n D}{\partial n_i} \right) \quad (4.41)$$

$$\text{and} \quad \frac{1}{RT} \left(\frac{1}{n} \frac{\partial n^2 a_m}{\partial n_i} \right) = D \frac{\partial n b_m}{\partial n_i} + b_m \frac{\partial n D}{\partial n_i} \quad (4.42)$$

The partial derivatives of Q and D are given by :

$$\left(\frac{1}{n} \frac{\partial n^2 Q}{\partial n_i} \right) = 2 \sum_{j=1}^m x_j \left(b - \frac{a}{RT} \right)_{ij} \quad (4.43)$$

$$\frac{\partial n D}{\partial n_i} = \frac{a_i}{b_i RT} + \frac{\ln \gamma_i^\infty}{\sigma} \quad (4.44)$$

with

$$\ln \gamma_i^\infty = \frac{1}{RT} \frac{\partial n a_\infty^E}{\partial n_i} \quad (4.45)$$

4.6 Block Diagrams

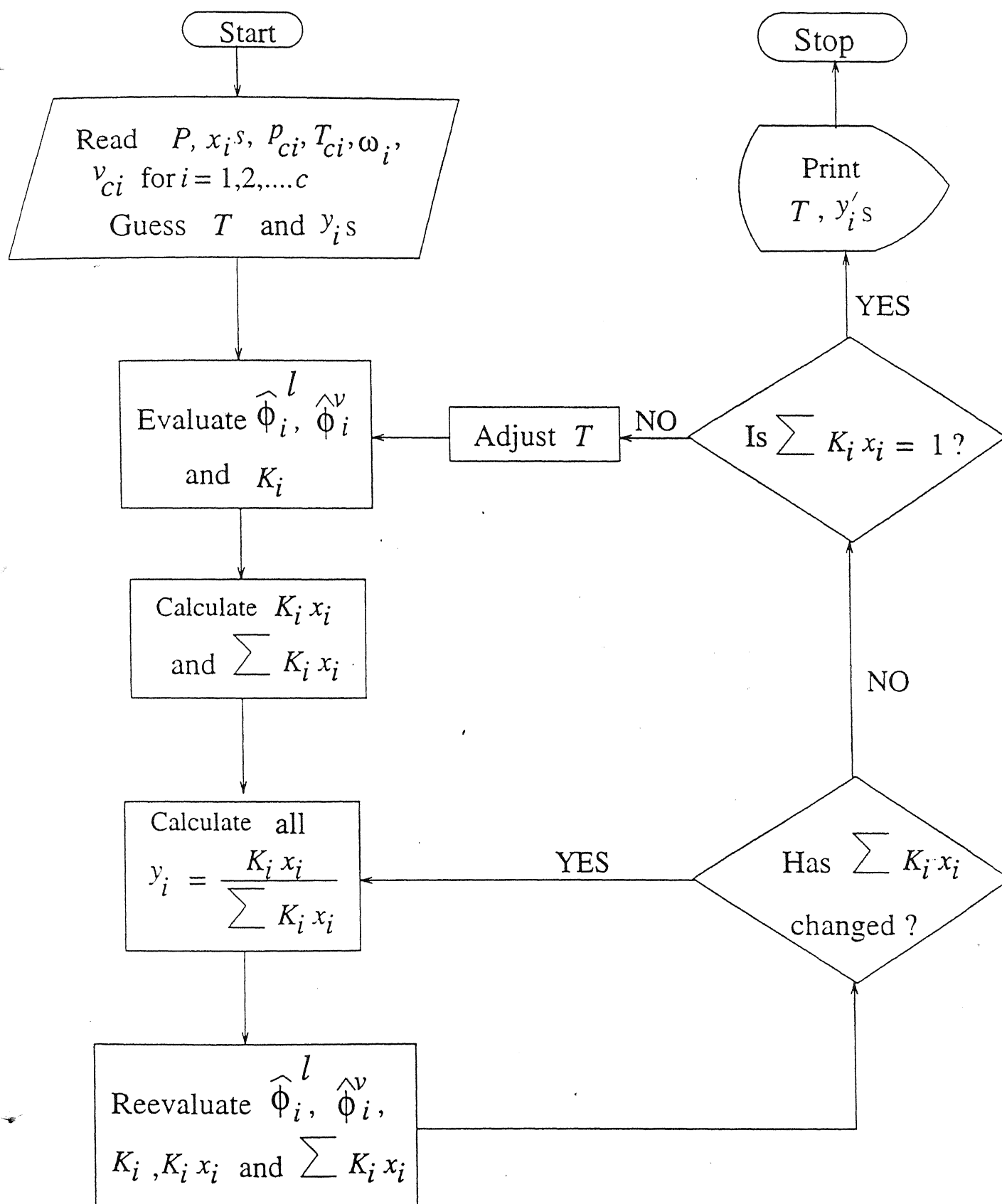


Figure 4.1 Algorithm for bubble temperature calculation using an Equation Of State

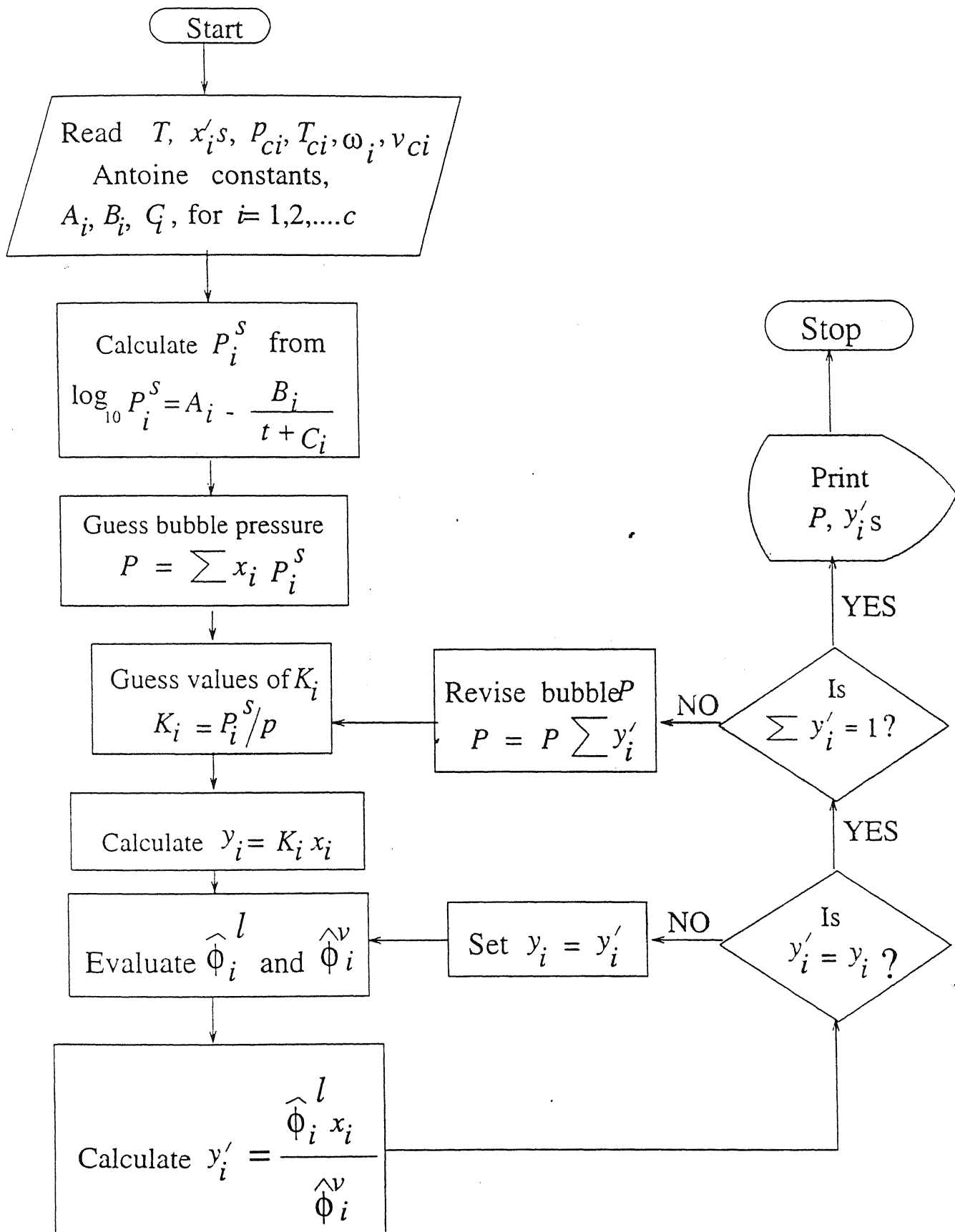


Figure 4.2 Algorithm for bubble pressure calculation using an Equation Of State

Chapter 5

RESULTS AND DISCUSSION

In the application of the analytic direct method for vapour-liquid equilibrium calculation, the success of the vapour-liquid equilibrium predictions depend on the accuracy of the equation of state and on the mixing rules that are used. The *PRSV* equation of state predicts vapour pressure of a component ~~more~~ more accurate than other existing cubic equations of state. The *Wong-Sandler* mixing rule is theoretically correct which is more accurate for a wider range of mixtures than other mixing models available. In the present work, the *Wong-Sandler* mixing rule along with the *PRSV* equation of state is used to predict VLE data for few binary and ternary systems through $\phi - \phi$ approach. In *Wong-Sandler* mixing rule, the *excess molar Helmholtz free energy* and the *activity coefficients* are calculated by *NRTL* model just because of its simplicity.

In the following pages, the results of 15 binary systems and 5 ternary systems of highly polar substances are presented in tabular form as well as graphical form. To test the applicability of this model to multicomponent systems, calculations have been performed for 5 ternary systems. The systems are so chosen such that each system contains at least one polar substance. The cross second virial coefficients B_{ij} are calculated by *Tsonopoulos correlation* in which binary interaction parameters for cross temperatures have been tuned in order to match calculated results with experimental results.

For a total of 20 systems, both BUBL P and BUBL T computations have been carried out. For BUBL P the computed equilibrium pressures have been compared with the experimental equilibrium pressures and for BUBL T the computed equilibrium temperatures have been compared with the experimental equilibrium temperatures and the deviations have been calculated. Similarly, the equilibrium vapour compositions have been compared with experimental equilibrium vapour compositions and the deviations in the vapour phase compositions have been determined. The experimental data have been taken from "Vapour liquid equilibrium data collection", DECHMA series and the data for critical properties have been taken from

5.1 Tables

| ACETONE --- BENZENE | | | | | | | |
|---------------------------------------|---------|--------|--------|--------|--------|--------|--------|
| PRESSURE OF THE SYSTEM (bar) | | | | | | | |
| 1.0130 | | | | | | | |
| CHANGED TSONOPOULOS-K VALUES | | | | | | | |
| .0000 .0000 | | | | | | | |
| .0000 .0000 | | | | | | | |
| TEMP (°C) | | X | | Y.exp | | Y.cal | |
| t(exp) | t(cal) | x1 | x2 | y1 | y2 | y1 | y2 |
| 80.1000 | 80.6000 | .0000 | 1.0000 | .0000 | 1.0000 | .0000 | 1.0000 |
| 79.2000 | 79.7000 | .0100 | .9900 | .0352 | .9648 | .0305 | .9695 |
| 76.3500 | 76.8000 | .0500 | .9500 | .1496 | .8504 | .1366 | .8634 |
| 73.6000 | 74.1000 | .1000 | .9000 | .2531 | .7469 | .2415 | .7585 |
| 69.7000 | 70.2000 | .2000 | .8000 | .4030 | .5970 | .3951 | .6049 |
| 66.7500 | 67.2000 | .3000 | .7000 | .5140 | .4860 | .5073 | .4927 |
| 64.5000 | 65.0000 | .4000 | .6000 | .6030 | .3970 | .5975 | .4025 |
| 62.6500 | 63.1000 | .5000 | .5000 | .6785 | .3215 | .6755 | .3245 |
| 61.0000 | 61.4000 | .6000 | .4000 | .7464 | .2536 | .7463 | .2537 |
| 59.6000 | 60.0000 | .7000 | .3000 | .8100 | .1900 | .8127 | .1873 |
| 58.3500 | 58.8500 | .8000 | .2000 | .8737 | .1263 | .8765 | .1235 |
| 57.2500 | 57.7000 | .9000 | .1000 | .9371 | .0629 | .9387 | .0613 |
| 56.7000 | 57.2000 | .9500 | .0500 | .9687 | .0313 | .9694 | .0306 |
| 56.2700 | 56.7000 | .9900 | .0100 | .9937 | .0063 | .9939 | .0061 |
| 56.1800 | 56.6000 | 1.0000 | .0000 | 1.0000 | .0000 | 1.0000 | .0000 |
| AVERAGE DEVIATION IN TEMPERATURE (°C) | | | | | | | |
| .463 | | | | | | | |
| AVERAGE DEVIATION IN Y-VALUES | | | | | | | |
| DY1 | | DY2 | | | | | |
| .00404 | | .00404 | | | | | |

Table 5.1.1: Comparison of experimental and calculated values of y_i and t from *Wong-Sandler* mixing rules for *Acetone-Benzene* at 1.013 bar pressure.

ACETONE --- CHLOROFORM
PRESSURE OF THE SYSTEM (bar)

1.0130

CHANGED TSONOPOULOS-K VALUES

.0000 .0000

.0000 .0000

| TEMP (°C) | | X | | Y.exp | | Y.cal | |
|-----------|---------|-------|-------|-------|-------|-------|-------|
| t(exp) | t(cal) | x1 | x2 | y1 | y2 | y1 | y2 |
| 62.8000 | 62.2000 | .1108 | .8892 | .0650 | .9350 | .0888 | .9112 |
| 63.1000 | 62.5000 | .1375 | .8625 | .1000 | .9000 | .1152 | .8848 |
| 63.8000 | 63.2000 | .2108 | .7892 | .1760 | .8240 | .1954 | .8046 |
| 64.4000 | 63.8000 | .2660 | .7340 | .2370 | .7630 | .2614 | .7386 |
| 63.9000 | 63.3000 | .4771 | .5229 | .5170 | .4830 | .5241 | .4759 |
| 62.8000 | 62.2000 | .5750 | .4250 | .6480 | .3520 | .6377 | .3623 |
| 61.6000 | 61.0000 | .6633 | .3367 | .7505 | .2495 | .7310 | .2690 |
| 60.4000 | 59.8000 | .7388 | .2612 | .8235 | .1765 | .8031 | .1969 |
| 59.4000 | 58.8000 | .7955 | .2045 | .8688 | .1312 | .8525 | .1475 |
| 58.8000 | 58.3500 | .8590 | .1410 | .9165 | .0835 | .9031 | .0969 |
| 57.5000 | 57.2000 | .9145 | .0855 | .9522 | .0478 | .9438 | .0562 |

AVERAGE DEVIATION IN TEMPERATURE (°C)

.559

AVERAGE DEVIATION IN Y-VALUES

DY1

DY2

.01620

.01620

Table 5.1.2: Comparison of experimental and calculated values of y_i and t from Wong-Sandler mixing rules for Acetone-Chloroform at 1.013 bar pressure.

ACETONE --- HEXANE
PRESSURE OF THE SYSTEM (bar)

1.0130

CHANGED TSONOPOULOS-K VALUES

.0000 .1550

.1550 .0000

| TEMP (°C) | | X | | Y.exp | | Y.cal | |
|-----------|---------|--------|--------|--------|--------|--------|--------|
| t(exp) | t(cal) | x1 | x2 | y1 | y2 | y1 | y2 |
| 68.7500 | 68.7500 | .0000 | 1.0000 | .0000 | 1.0000 | .0000 | 1.0000 |
| 58.9100 | 59.0000 | .0942 | .9058 | .3350 | .6650 | .3337 | .6663 |
| 53.5100 | 53.6000 | .1986 | .8014 | .4830 | .5170 | .4853 | .5147 |
| 51.5700 | 51.6000 | .2989 | .7011 | .5400 | .4600 | .5562 | .4438 |
| 50.5400 | 50.5700 | .3983 | .6017 | .5840 | .4160 | .5958 | .4042 |
| 50.0000 | 50.1000 | .4995 | .5005 | .6100 | .3900 | .6208 | .3792 |
| 49.7800 | 49.8000 | .5999 | .4001 | .6160 | .3840 | .6395 | .3605 |
| 49.8400 | 49.8400 | .6999 | .3001 | .6540 | .3460 | .6607 | .3393 |
| 50.3100 | 50.3500 | .8007 | .1993 | .7000 | .3000 | .6978 | .3022 |
| 51.7600 | 51.8000 | .9015 | .0985 | .7950 | .2050 | .7809 | .2191 |
| 56.2500 | 56.3000 | 1.0000 | .0000 | 1.0000 | .0000 | 1.0000 | .0000 |

AVERAGE DEVIATION IN TEMPERATURE (°C)

.045

AVERAGE DEVIATION IN Y-VALUES

DY1

DY2

.00808

.00808

Table 5.1.3: Comparison of experimental and calculated values of y_i and t from *Wong-Sandler* mixing rules for *Acetone-Hexane* at 1.013 bar pressure.

ACETONE --- METHANOL
PRESSURE OF THE SYSTEM (bar)

1.0130

CHANGED TSONOPOULOS-K VALUES

.0000 .0500

.0500 .0000

| TEMP (°C) | | X | | Y.exp | | Y.cal | |
|-----------|---------|-------|-------|-------|-------|-------|-------|
| t(exp) | t(cal) | x1 | x2 | y1 | y2 | y1 | y2 |
| 62.8000 | 62.9000 | .0600 | .9400 | .0970 | .9030 | .1127 | .8873 |
| 60.8000 | 60.8000 | .1500 | .8500 | .2500 | .7500 | .2503 | .7497 |
| 58.6000 | 58.7000 | .2950 | .7050 | .4200 | .5800 | .4181 | .5819 |
| 57.2000 | 57.3000 | .3980 | .6020 | .5170 | .4830 | .5127 | .4873 |
| 56.3000 | 56.3000 | .5250 | .4750 | .6250 | .3750 | .6115 | .3885 |
| 55.8000 | 55.8500 | .7320 | .2680 | .7540 | .2460 | .7548 | .2452 |
| 55.7000 | 55.8000 | .8000 | .2000 | .8000 | .2000 | .8040 | .1960 |
| 55.9000 | 56.0000 | .8920 | .1080 | .8750 | .1250 | .8795 | .1205 |

AVERAGE DEVIATION IN TEMPERATURE (°C)

.069

AVERAGE DEVIATION IN Y-VALUES

DY1

DY2

.00563

.00563

Table 5.1.4: Comparison of experimental and calculated values of y_i and t from Wong-Sandler mixing rules for Acetone-Methanol at 1.013 bar pressure.

ACETONE --- TETRACHLOROMETHANE
PRESSURE OF THE SYSTEM (bar)

1.0130

CHANGED TSONOPOULOS-K VALUES

.0000 .0000

.0000 .0000

| TEMP(°C) | | X | | Y.exp | | Y.cal | |
|----------|---------|-------|-------|-------|-------|-------|-------|
| t(exp) | t(cal) | x1 | x2 | y1 | y2 | y1 | y2 |
| 70.8000 | 70.9000 | .0590 | .9410 | .2025 | .7975 | .1753 | .8247 |
| 68.7400 | 68.8000 | .0870 | .9130 | .2710 | .7290 | .2369 | .7631 |
| 64.4500 | 64.5000 | .1790 | .8210 | .4075 | .5925 | .3827 | .6173 |
| 61.9100 | 62.0000 | .2640 | .7360 | .4895 | .5105 | .4739 | .5261 |
| 59.8300 | 59.9000 | .3740 | .6260 | .5655 | .4345 | .5626 | .4374 |
| 58.7400 | 58.8000 | .4510 | .5490 | .6125 | .3875 | .6149 | .3851 |
| 57.9400 | 58.0000 | .5255 | .4745 | .6550 | .3450 | .6619 | .3381 |
| 57.1800 | 57.3000 | .6165 | .3835 | .7065 | .2935 | .7179 | .2821 |
| 56.6700 | 56.8000 | .6960 | .3040 | .7560 | .2440 | .7678 | .2322 |
| 56.3600 | 56.4500 | .7620 | .2380 | .7985 | .2015 | .8112 | .1888 |
| 56.1500 | 56.3000 | .8295 | .1705 | .8460 | .1540 | .8586 | .1414 |
| 56.0100 | 56.2500 | .8950 | .1050 | .8980 | .1020 | .9086 | .0914 |
| 56.0200 | 56.0320 | .9140 | .0860 | .9150 | .0850 | .9240 | .0760 |
| 55.9900 | 56.1500 | .9530 | .0470 | .9520 | .0480 | .9571 | .0429 |

AVERAGE DEVIATION IN TEMPERATURE (°C)

.099

AVERAGE DEVIATION IN Y-VALUES

DY1

DY2

.01336

.01336

Table 5.1.5: Comparison of experimental and calculated values of y_i and t from Wong-Sandler mixing rules for Acetone-Tetrachloromethane at 1.013 bar pressure.

CARBON DISULPHIDE --- ACETONE
PRESSURE OF THE SYSTEM (bar)

1.0130

CHANGED TSONOPOULOS-K VALUES

.0000 .1000

.1000 .0000

| TEMP (°C) | | X | | Y.exp | | Y.cal | |
|-----------|---------|-------|-------|-------|-------|-------|-------|
| t(exp) | t(cal) | x1 | x2 | y1 | y2 | y1 | y2 |
| 54.0000 | 54.0000 | .0190 | .9810 | .0832 | .9168 | .0752 | .9248 |
| 51.4000 | 51.4500 | .0476 | .9524 | .1850 | .8150 | .1682 | .8318 |
| 46.6000 | 46.6000 | .1340 | .8660 | .3510 | .6490 | .3532 | .6468 |
| 44.0000 | 44.1000 | .1958 | .8042 | .4430 | .5570 | .4352 | .5648 |
| 41.4000 | 41.5000 | .2912 | .7088 | .5275 | .4725 | .5193 | .4807 |
| 40.3000 | 40.4000 | .3798 | .6202 | .5740 | .4260 | .5704 | .4296 |
| 39.8000 | 39.9500 | .4477 | .5523 | .5980 | .4020 | .5994 | .4006 |
| 39.3000 | 39.4500 | .5360 | .4640 | .6270 | .3730 | .6291 | .3709 |
| 39.1000 | 39.2500 | .6530 | .3470 | .6610 | .3390 | .6614 | .3386 |
| 39.3000 | 39.4000 | .7894 | .2106 | .7050 | .2950 | .7043 | .2957 |
| 39.6000 | 39.7000 | .8023 | .1977 | .7230 | .2770 | .7098 | .2902 |
| 40.5000 | 40.5500 | .8795 | .1205 | .7600 | .2400 | .7573 | .2427 |
| 43.5000 | 43.5500 | .9683 | .0317 | .8860 | .1140 | .8915 | .1085 |

AVERAGE DEVIATION IN TEMPERATURE (°C)

.085

AVERAGE DEVIATION IN Y-VALUES

DY1

DY2

.00557

.00557

Table 5.1.6: Comparison of experimental and calculated values of y_i and t from *Wong-Sandler* mixing rules for *Carbon disulfide-Acetone* at 1.013 bar pressure.

ETHYLENE OXIDE --- ACETALDEHYDE
PRESSURE OF THE SYSTEM (bar)

1.0130

CHANGED TSONOPOULOS-K VALUES

.0000 .0200

.0200 .0000

| TEMP(°C) | | X | | Y.exp | | Y.cal | |
|----------|---------|-------|-------|-------|-------|-------|-------|
| t(exp) | t(cal) | x1 | x2 | y1 | y2 | y1 | y2 |
| 17.3000 | 17.3000 | .2950 | .7050 | .3900 | .6100 | .3896 | .6104 |
| 16.0000 | 16.0000 | .4100 | .5900 | .5130 | .4870 | .5135 | .4865 |
| 14.6000 | 14.6000 | .5280 | .4720 | .6360 | .3640 | .6282 | .3718 |
| 13.5000 | 13.5000 | .6400 | .3600 | .7200 | .2800 | .7272 | .2728 |
| 11.6000 | 11.6000 | .8830 | .1170 | .9180 | .0820 | .9172 | .0828 |
| 10.7000 | 10.7000 | .9666 | .0334 | .9792 | .0208 | .9768 | .0232 |
| 10.7000 | 10.7000 | .9675 | .0325 | .9778 | .0222 | .9775 | .0225 |
| 10.6000 | 10.6000 | .9794 | .0206 | .9861 | .0139 | .9857 | .0143 |
| 10.6000 | 10.6000 | .9852 | .0148 | .9908 | .0092 | .9898 | .0102 |
| 10.6000 | 10.6000 | .9877 | .0123 | .9912 | .0088 | .9915 | .0085 |
| 10.6000 | 10.6000 | .9895 | .0105 | .9930 | .0070 | .9927 | .0073 |
| 10.6000 | 10.6000 | .9912 | .0088 | .9947 | .0053 | .9939 | .0061 |
| 10.4000 | 10.4000 | .9917 | .0083 | .9956 | .0044 | .9943 | .0057 |
| 10.4000 | 10.4000 | .9965 | .0035 | .9982 | .0018 | .9976 | .0024 |

AVERAGE DEVIATION IN TEMPERATURE (°C)

.000

AVERAGE DEVIATION IN Y-VALUES

DY1

DY2

.00172

.00172

Table 5.1.7: Comparison of experimental and calculated values of y_i and t from Wong-Sandler mixing rules for Ethylene oxide-Acetaldehyde at 1.013 bar pressure.

ACETALDEHYDE --- ACETIC ACID
PRESSURE OF THE SYSTEM (bar)

1.0240

CHANGED TSONOPOULOS-K VALUES

.0000 .0000

.0000 .0000

| TEMP (°C) | | X | | Y.exp | | Y.cal | |
|-----------|---------|-------|-------|-------|-------|-------|-------|
| t(exp) | t(cal) | x1 | x2 | y1 | y2 | y1 | y2 |
| 84.0000 | 82.0000 | .0900 | .9100 | .6380 | .3620 | .7344 | .2656 |
| 68.0000 | 63.5000 | .1830 | .8170 | .8080 | .1920 | .8860 | .1140 |
| 58.0000 | 55.5000 | .2460 | .7540 | .8790 | .1210 | .9250 | .0750 |
| 50.0000 | 49.0000 | .3090 | .6910 | .9270 | .0730 | .9474 | .0526 |
| 42.0000 | 42.0000 | .4190 | .5810 | .9660 | .0340 | .9681 | .0319 |

AVERAGE DEVIATION IN TEMPERATURE (°C)

2.000

AVERAGE DEVIATION IN Y-VALUES

DY1

DY2

.04857

.04857

Table 5.1.8: Comparison of experimental and calculated values of y_i and t from Wong-Sandler mixing rules for Acetaldehyde-Acetic acid at 1.024 bar pressure.

ACETALDEHYDE --- BENZENE

PRESSURE OF THE SYSTEM (bar)

1.0130

CHANGED TSONOPOULOS-K VALUES

.0000 .0300

.0300 .0000

| TEMP (°C) | | X | | Y.exp | | Y.cal | |
|-----------|---------|--------|--------|--------|--------|--------|--------|
| t(exp) | t(cal) | x1 | x2 | y1 | y2 | y1 | y2 |
| 80.1000 | 80.6500 | .0000 | 1.0000 | .0000 | 1.0000 | .0000 | 1.0000 |
| 71.0000 | 71.0000 | .0500 | .9500 | .3130 | .6870 | .3231 | .6769 |
| 63.0000 | 62.7500 | .1000 | .9000 | .5220 | .4780 | .4926 | .5074 |
| 54.2000 | 53.0000 | .2000 | .8000 | .6940 | .3060 | .6692 | .3308 |
| 49.4000 | 47.0000 | .3000 | .7000 | .7670 | .2330 | .7671 | .2329 |
| 46.2000 | 42.0000 | .4000 | .6000 | .8160 | .1840 | .8341 | .1659 |
| 44.0000 | 37.0000 | .5000 | .5000 | .8540 | .1460 | .8842 | .1158 |
| 42.0000 | 33.0000 | .6000 | .4000 | .8870 | .1130 | .9219 | .0781 |
| 39.8000 | 30.0000 | .7000 | .3000 | .9160 | .0840 | .9502 | .0498 |
| 37.7000 | 26.3000 | .8000 | .2000 | .9440 | .0560 | .9719 | .0281 |
| 36.0000 | 23.5000 | .9000 | .1000 | .9680 | .0320 | .9880 | .0120 |
| 20.8000 | 21.5000 | 1.0000 | .0000 | 1.0000 | .0000 | 1.0000 | .0000 |

AVERAGE DEVIATION IN TEMPERATURE (°C)

4.916

AVERAGE DEVIATION IN Y-VALUES

DY1 DY2

.01915 .01915

Table 5.1.9: Comparison of experimental and calculated values of y_i and t from *Wong-Sandler* mixing rules for *Acetaldehyde-Benzene* at 1.013 bar pressure.

DIETHYL ETHER --- BENZENE
PRESSURE OF THE SYSTEM (bar)

1.0160

CHANGED TSONOPOULOS-K VALUES

.0000 .0000

.0000 .0000

| TEMP(°C) | | X | | Y.exp | | Y.cal | |
|----------|---------|--------|--------|--------|--------|--------|--------|
| t(exp) | t(cal) | x1 | x2 | y1 | y2 | y1 | y2 |
| 80.3000 | 80.3200 | .0000 | 1.0000 | .0000 | 1.0000 | .0000 | 1.0000 |
| 67.5000 | 67.5000 | .1755 | .8245 | .4601 | .5399 | .4712 | .5288 |
| 60.6500 | 60.6700 | .2825 | .7175 | .6295 | .3705 | .6328 | .3672 |
| 55.9500 | 55.9500 | .3691 | .6309 | .7269 | .2731 | .7257 | .2743 |
| 52.0000 | 52.0500 | .4520 | .5480 | .7967 | .2033 | .7930 | .2070 |
| 50.0500 | 50.0300 | .4991 | .5009 | .8288 | .1712 | .8243 | .1757 |
| 48.5000 | 48.4700 | .5391 | .4609 | .8525 | .1475 | .8476 | .1524 |
| 47.8000 | 47.8400 | .5490 | .4510 | .8580 | .1420 | .8533 | .1467 |
| 46.1000 | 46.1200 | .5987 | .4013 | .8831 | .1169 | .8780 | .1220 |
| 44.3500 | 44.3800 | .6520 | .3480 | .9063 | .0937 | .9011 | .0989 |
| 42.3000 | 42.2500 | .7177 | .2823 | .9307 | .0693 | .9257 | .0743 |
| 38.1500 | 38.2000 | .8623 | .1377 | .9718 | .0282 | .9682 | .0318 |
| 34.7500 | 34.8000 | 1.0000 | .0000 | 1.0000 | .0000 | 1.0000 | .0000 |

AVERAGE DEVIATION IN TEMPERATURE (°C)

.029

AVERAGE DEVIATION IN Y-VALUES

DY1

DY2

.00402

.00402

Table 5.1.10: Comparison of experimental and calculated values of y_i and t from Wong-Sandler mixing rules for *Diethyl ether-Benzene* at 1.016 bar pressure.

DIETHYL ETHER --- CHLOROFORM

TEMPERATURE OF THE SYSTEM (K)

290.0000

CHANGED TSONOPOULOS-K VALUES

.0000 .0000

.0000 .0000

| PRESS. (mm) | | X | | Y.exp | | Y.cal | |
|-------------|---------|--------|-------|--------|-------|--------|-------|
| P(exp) | P(cal) | x1 | x2 | y1 | y2 | y1 | y2 |
| 143.000 | 146.517 | .1000 | .9000 | .0980 | .9020 | .1281 | .8718 |
| 143.000 | 155.016 | .2000 | .8000 | .2240 | .7760 | .2899 | .7100 |
| 151.000 | 170.068 | .3000 | .7000 | .3970 | .6030 | .4602 | .5395 |
| 166.000 | 191.833 | .4000 | .6000 | .5720 | .4280 | .6146 | .3847 |
| 193.000 | 219.648 | .5000 | .5000 | .7410 | .2590 | .7395 | .2595 |
| 230.000 | 252.208 | .6000 | .4000 | .8520 | .1480 | .8331 | .1657 |
| 273.000 | 287.813 | .7000 | .3000 | .9190 | .0810 | .8999 | .0990 |
| 317.000 | 324.650 | .8000 | .2000 | .9590 | .0410 | .9465 | .0528 |
| 360.000 | 361.019 | .9000 | .1000 | .9830 | .0170 | .9785 | .0213 |
| 397.000 | 395.544 | 1.0000 | .0000 | 1.0000 | .0000 | 1.0000 | .0000 |

AVERAGE DEVIATION IN PRESSURE(mm Hg)

13.42331

AVERAGE DEVIATION IN Y-VALUES

DY1

DY2

0.02583

0.02553

Table 5.1.11: Comparison of experimental and calculated values of y_i and p from Wong-Sandler mixing rules for *Diethyl ether-Chloroform* at 290.0 K temperature.

DIETHYL ETHER --- CARBON DISULFIDE

TEMPERATURE OF THE SYSTEM (K)

293.0000

CHANGED TSONOPOULOS-K VALUES

.0000 .0000

.0000 .0000

| PRESS. (mm) | | X | | Y.exp | | Y.cal | |
|-------------|---------|--------|-------|--------|-------|--------|-------|
| P(exp) | P(cal) | x1 | x2 | y1 | y2 | y1 | y2 |
| 366.000 | 335.954 | .1500 | .8500 | .2760 | .7240 | .2738 | .7292 |
| 393.000 | 359.761 | .2500 | .7500 | .3820 | .6180 | .3878 | .6158 |
| 421.000 | 386.673 | .4000 | .6000 | .5060 | .4940 | .5219 | .4818 |
| 432.000 | 400.916 | .5000 | .5000 | .5790 | .4210 | .6008 | .4025 |
| 443.000 | 418.475 | .6500 | .3500 | .6750 | .3250 | .7152 | .2873 |
| 445.000 | 432.309 | .8000 | .2000 | .8020 | .1980 | .8321 | .1695 |
| 446.000 | 439.636 | .9000 | .1000 | .8990 | .1010 | .9140 | .0870 |
| 441.000 | 445.464 | 1.0000 | .0000 | 1.0000 | .0000 | 1.0000 | .0000 |

AVERAGE DEVIATION IN PRESSURE(mm Hg)

21.88020

AVERAGE DEVIATION IN Y-VALUES

DY1

DY2

0.015822

0.014288

Table 5.1.12: Comparison of experimental and calculated values of y_i and p from Wong-Sandler mixing rules for *Diethyl ether-Carbon disulfide* at 293.0 K temperature.

DIETHYL ETHER ----- ETHYL ACETATE
 TEMPERATURE OF THE SYSTEM (K)

303.0000

CHANGED TSONOPOULOS-K VALUES

.0000 .0000

.0000 .0000

| PRESS.(mm) | | X | | Y.exp | | Y.cal | |
|------------|---------|--------|-------|--------|-------|--------|-------|
| P(exp) | P(cal) | x1 | x2 | y1 | y2 | y1 | y2 |
| 227.000 | 233.558 | .2000 | .8000 | .5758 | .4242 | .5749 | .4265 |
| 281.000 | 288.416 | .3000 | .7000 | .7012 | .2988 | .6974 | .3038 |
| 333.000 | 342.573 | .4000 | .6000 | .7859 | .2141 | .7803 | .2208 |
| 388.500 | 395.731 | .5000 | .5000 | .8465 | .1535 | .8400 | .1609 |
| 441.000 | 447.736 | .6000 | .4000 | .8918 | .1082 | .8853 | .1155 |
| 494.000 | 498.624 | .7000 | .3000 | .9268 | .0732 | .9212 | .0795 |
| 545.000 | 548.688 | .8000 | .2000 | .9550 | .0450 | .9509 | .0496 |
| 597.000 | 598.563 | .9000 | .1000 | .9787 | .0213 | .9766 | .0237 |
| 650.000 | 644.499 | 1.0000 | .0000 | 1.0000 | .0000 | 1.0075 | .0000 |

AVERAGE DEVIATION IN PRESSURE(mm Hg)

5.87954

AVERAGE DEVIATION IN Y-VALUES

DY1

DY2

.00445

.00426

Table 5.1.13: Comparison of experimental and calculated values of y_i and p from Wong-Sandler mixing rules for *Diethyl ether-Ethyl acetate* at 303.0 K temperature.

ETHYL CHLORIDE ---- DIETHYL ETHER
TEMPERATURE OF THE SYSTEM (K)

298.0000

CHANGED TSONOPOULOS-K VALUES

.0000 .0400

.0400 .0000

| PRESS. (mm) | | X | | Y.exp | | Y.cal | |
|-------------|----------|--------|-------|--------|-------|-------|-------|
| P(exp) | P(cal) | x1 | x2 | y1 | y2 | y1 | y2 |
| 967.000 | 963.354 | .4530 | .5470 | .6667 | .3333 | .6669 | .3381 |
| 1004.000 | 1006.177 | .5210 | .4790 | .7088 | .2912 | .7116 | .2932 |
| 1075.000 | 1098.921 | .7000 | .3000 | .8068 | .1932 | .8124 | .1913 |
| 1150.000 | 1179.886 | .9200 | .0800 | .8346 | .1654 | .9389 | .0623 |
| 1162.000 | 1200.012 | 1.0000 | .0000 | 1.0000 | .0000 | .9985 | .0000 |

AVERAGE DEVIATION IN PRESSURE(mm Hg)

16.97869

AVERAGE DEVIATION IN Y-VALUES

DY1 DY2

.01909 .01945

Table 5.1.14: Comparison of experimental and calculated values of y_i and p from Wong-Sandler mixing rules for *Ethyl chloride-Diethyl ether* at 298.0 K temperature.

METHANOL --- ETHANOL
PRESSURE OF THE SYSTEM (bar)

1.0130

CHANGED TSONOPOULOS-K VALUES

.0000 .0150

.0150 .0000

| TEMP(°C) | | X | | Y.exp | | Y.cal | |
|----------|---------|-------|-------|-------|-------|-------|-------|
| t(exp) | t(cal) | x1 | x2 | y1 | y2 | y1 | y2 |
| 77.0000 | 77.0000 | .0730 | .9270 | .1200 | .8800 | .1121 | .8879 |
| 75.8000 | 75.8000 | .1420 | .8580 | .2220 | .7780 | .2108 | .7892 |
| 74.0000 | 74.0000 | .2480 | .7520 | .3620 | .6380 | .3500 | .6500 |
| 72.3000 | 72.3000 | .3750 | .6250 | .5050 | .4950 | .4987 | .5013 |
| 70.9000 | 70.9000 | .4700 | .5300 | .6000 | .4000 | .5986 | .4014 |
| 69.2000 | 69.2000 | .6000 | .4000 | .7250 | .2750 | .7204 | .2796 |
| 67.6000 | 67.6000 | .7250 | .2750 | .8200 | .1800 | .8226 | .1774 |
| 65.8000 | 66.0000 | .8880 | .1120 | .9320 | .0680 | .9352 | .0648 |

AVERAGE DEVIATION IN TEMPERATURE (°C)

.025

AVERAGE DEVIATION IN Y-VALUES,

DY1

DY2

.00616

.00616

Table 5.1.15: Comparison of experimental and calculated values of y_i and p from Wong-Sandler mixing rules for *Methanol-Ethanol* at 1.013 bar pressure.

ACETONE --- CHLOROFORM --- HEXANE

TEMPERATURE OF THE SYSTEM (K)

308.0000

CHANGED TSONOPOULOS-K VALUES

.0000 .0000 .1500

.0000 .0000 .1000

.1500 .1000 .0000

| PRES. (mm) | | X | | Y.exp | | Y.cal | |
|------------|----------|-------|-------|-------|-------|-------|-------|
| P(exp) | P(cal) | x1 | x2 | y1 | y2 | y1 | y2 |
| 300.5000 | 319.4629 | .0650 | .6000 | .0600 | .6000 | .0643 | .6022 |
| 320.9000 | 315.3640 | .0870 | .1000 | .2670 | .0890 | .2667 | .1277 |
| 287.0000 | 305.3841 | .1090 | .7990 | .0600 | .7930 | .0779 | .7771 |
| 280.1000 | 301.0839 | .2070 | .7000 | .1580 | .6790 | .1768 | .6570 |
| 275.6000 | 306.1683 | .3050 | .6010 | .2760 | .5450 | .2894 | .5222 |
| 344.3000 | 361.7745 | .4000 | .3040 | .4620 | .1840 | .4512 | .1985 |
| 340.7000 | 360.8897 | .4980 | .3050 | .5410 | .1730 | .5119 | .1878 |
| 413.9000 | 411.1522 | .5990 | .1030 | .6210 | .0420 | .6081 | .0491 |
| 401.7000 | 404.5984 | .7100 | .1070 | .6690 | .0430 | .6553 | .0500 |
| 383.2000 | 383.8397 | .8070 | .1040 | .7520 | .0440 | .7401 | .0516 |

AVERAGE DEVIATION IN PRESSURE(mm Hg)

13.83855

AVERAGE DEVIATION IN Y-VALUES

| DY1 | DY2 | DY3 |
|--------|--------|--------|
| .01331 | .01575 | .00940 |

Table 5.1.16: Comparison of experimental and calculated values of y_i and p from Wong-Sandler mixing rules for *Acetone-Chloroform-Hexane* at 308.0 K temperature.

ACETONE --- CHLOROFORM --- TOLUENE
PRESSURE OF THE SYSTEM (bar)

1.0130

CHANGED TSONOPOULOS-K VALUES

| | | |
|-------|-------|-------|
| .0000 | .1000 | .1700 |
| .1000 | .0000 | .0000 |
| .1700 | .0000 | .0000 |

| TEMP. (°C) | | X | | Y.exp | | Y.cal | |
|------------|---------|-------|-------|-------|-------|-------|-------|
| t(exp) | t(cal) | x1 | x2 | y1 | y2 | y1 | y2 |
| 88.8000 | 84.5000 | .1000 | .1000 | .4130 | .1720 | .4030 | .2224 |
| 78.4000 | 74.0000 | .2000 | .2000 | .5180 | .2670 | .4980 | .2957 |
| 69.4000 | 64.5000 | .2000 | .6000 | .2650 | .7000 | .2856 | .6546 |
| 70.3000 | 65.0000 | .3000 | .4000 | .4860 | .4330 | .4725 | .4370 |
| 68.5000 | 64.0000 | .4000 | .3000 | .6270 | .2850 | .6019 | .3079 |
| 66.6000 | 62.5000 | .5000 | .2000 | .7660 | .1600 | .7149 | .1943 |
| 64.8000 | 62.0000 | .6000 | .1000 | .8540 | .0640 | .8144 | .0929 |
| 62.4000 | 60.0000 | .7000 | .1000 | .8880 | .0610 | .8430 | .0897 |
| 61.8000 | 59.5000 | .7000 | .2000 | .8450 | .1320 | .7849 | .1793 |
| 60.4000 | 58.5000 | .8000 | .1000 | .9170 | .0600 | .8732 | .0889 |

AVERAGE DEVIATION IN TEMPERATURE (°C)

3.690

AVERAGE DEVIATION IN Y-VALUES

| DY1 | DY2 | DY3 |
|--------|--------|--------|
| .03291 | .03195 | .01571 |

Table 5.1.17: Comparison of experimental and calculated values of y_i and t from Wong-Sandler mixing rules for Acetone-Chloroform-Toluene at 1.013 bar pressure.

ACETONE --- TETRACHLOROMETHANE --- BENZENE
PRESSURE OF THE SYSTEM (bar)

1.0130

CHANGED TSONOPOULOS-K VALUES

.0000 .0000 .0500

.0000 .0000 .0500

.0500 .0500 .0000

| TEMP. (°C) | | X | | Y.exp | | Y.cal | |
|------------|---------|-------|-------|-------|-------|-------|-------|
| t(exp) | t(cal) | x1 | x2 | y1 | y2 | y1 | y2 |
| 79.7000 | 79.5000 | .0160 | .0170 | .0523 | .0200 | .0516 | .0253 |
| 75.3000 | 74.2500 | .0520 | .2630 | .1450 | .2580 | .1376 | .2917 |
| 65.8000 | 68.0000 | .1410 | .7990 | .3460 | .6140 | .3204 | .6275 |
| 65.1000 | 65.0000 | .2880 | .2860 | .4800 | .2100 | .4748 | .2415 |
| 64.2000 | 64.5000 | .3130 | .2440 | .5240 | .2100 | .5009 | .2082 |
| 63.0000 | 62.5000 | .4700 | .0910 | .6320 | .0830 | .6424 | .0801 |
| 60.1000 | 60.2000 | .5600 | .1960 | .6740 | .1760 | .6856 | .1584 |
| 58.5000 | 59.5000 | .5400 | .4310 | .6820 | .3030 | .6653 | .3151 |
| 58.3000 | 59.0000 | .6310 | .2960 | .7320 | .2280 | .7243 | .2273 |
| 57.5000 | 58.0000 | .7420 | .1770 | .7950 | .1600 | .8017 | .1440 |
| 57.4000 | 57.4000 | .8570 | .0630 | .8860 | .0620 | .8899 | .0550 |
| 57.4000 | 57.4000 | .7840 | .1860 | .8260 | .1260 | .8280 | .1515 |

AVERAGE DEVIATION IN TEMPERATURE (°C)

.554

AVERAGE DEVIATION IN Y-VALUES

| | | |
|--------|--------|--------|
| DY1 | DY2 | DY3 |
| .00839 | .01378 | .01155 |

Table 5.1.18: Comparison of experimental and calculated values of y_i and t from Wong-Sandler mixing rules for Acetone-Tetrachloromethane-Benzene at 1.013 bar pressure.

METHANOL --- HEPTANE ---TOLUENE
 PRESSURE OF THE SYSTEM (bar)

1.0130

CHANGED TSONOPOULOS-K VALUES

| | | |
|-------|-------|-------|
| .0000 | .3000 | .1500 |
| .3000 | .0000 | .0000 |
| .1500 | .0000 | .0000 |

| TEMP. (°C) | | X | | Y.exp | | Y.cal | |
|------------|---------|-------|-------|-------|-------|-------|-------|
| t(exp) | t(cal) | x1 | x2 | y1 | y2 | y1 | y2 |
| 62.9600 | 64.0000 | .3172 | .2533 | .7458 | .1826 | .7665 | .1199 |
| 63.3400 | 64.5000 | .3711 | .0962 | .7797 | .0635 | .7888 | .0615 |
| 59.9700 | 59.5000 | .5409 | .3412 | .7520 | .2043 | .7973 | .1692 |
| 61.3500 | 60.5000 | .6038 | .1717 | .7697 | .1412 | .7926 | .1318 |
| 62.5100 | 62.5100 | .6114 | .0911 | .7864 | .0911 | .8048 | .0867 |
| 61.5900 | 61.5900 | .7494 | .0787 | .7927 | .1123 | .7956 | .1183 |
| 59.9600 | 59.5000 | .7733 | .1510 | .7563 | .1969 | .7647 | .1986 |
| 60.7700 | 60.0000 | .8486 | .0684 | .7815 | .1517 | .7824 | .1604 |

AVERAGE DEVIATION IN TEMPERATURE (°C)

0.596

AVERAGE DEVIATION IN Y-VALUES

| DY1 | DY2 | DY3 |
|--------|---------|--------|
| .01609 | .016252 | .01443 |

Table 5.1.19: Comparison of experimental and calculated values of y_i and t from Wong-Sandler mixing rules for *Methanol-Heptane-Toluene* at 1.013 bar pressure.

METHANOL - TETRACHLOROMETHANE --- BENZENE

TEMPERATURE OF THE SYSTEM (K)

307.6800

CHANGED TSONOPOULOS-K VALUES

.0000 .1500 .1500

.1500 .0000 .0000

.1500 .0000 .0000

| PRESS. (mm) | | X | | Y.exp | | Y.cal | |
|-------------|----------|-------|-------|-------|-------|-------|-------|
| P(exp) | P(cal) | x1 | x2 | y1 | y2 | y1 | y2 |
| 291.1100 | 284.8949 | .2075 | .1900 | .4920 | .1472 | .5077 | .1538 |
| 302.1300 | 294.5722 | .2110 | .3879 | .4804 | .2774 | .4829 | .2911 |
| 308.6300 | 300.1083 | .1987 | .5876 | .4733 | .3999 | .4681 | .4058 |
| 307.2300 | 307.4335 | .3781 | .3122 | .5043 | .2747 | .5284 | .2697 |
| 308.1300 | 308.2517 | .5543 | .2078 | .5308 | .2501 | .5512 | .2425 |
| 298.8000 | 302.2973 | .7599 | .1076 | .5903 | .2080 | .5945 | .2145 |

AVERAGE DEVIATION IN PRESSURE(mm Hg)

4.35286

AVERAGE DEVIATION IN Y-VALUES

| | | |
|--------|--------|--------|
| DY1 | DY2 | DY3 |
| .01201 | .00755 | .01115 |

Table 5.1.20: Comparison of experimental and calculated values of y_i and p from Wong-Sandler mixing rules for *Methanol-Tetrachloromethane-Benzene* at 307.68 K temperature.

5.2 Figures

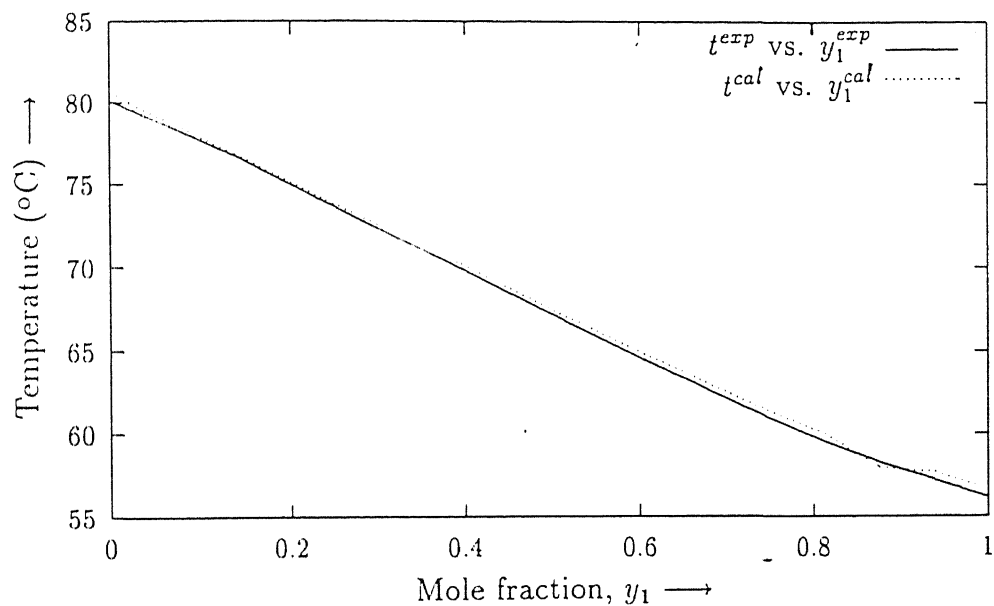


Figure 5.2.1: Comparison of experimental and calculated values of y_i and t from Wong-Sandler mixing rules for *Acetone-Benzene* at 1.013 bar pressure.

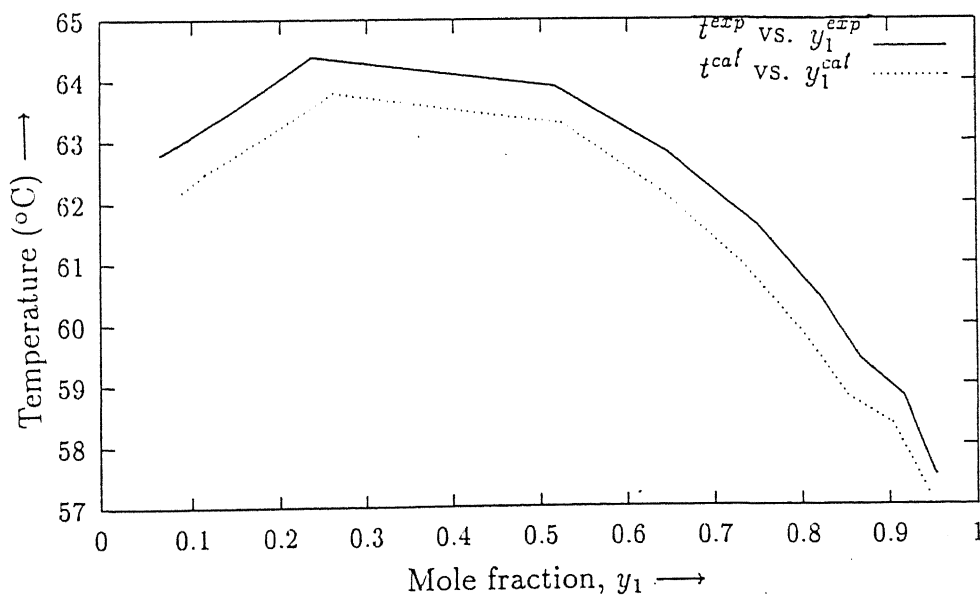


Figure 5.2.2: Comparison of experimental and calculated values of y_i and t from Wong-Sandler mixing rules for *Acetone-Chloroform* at 1.013 bar pressure.

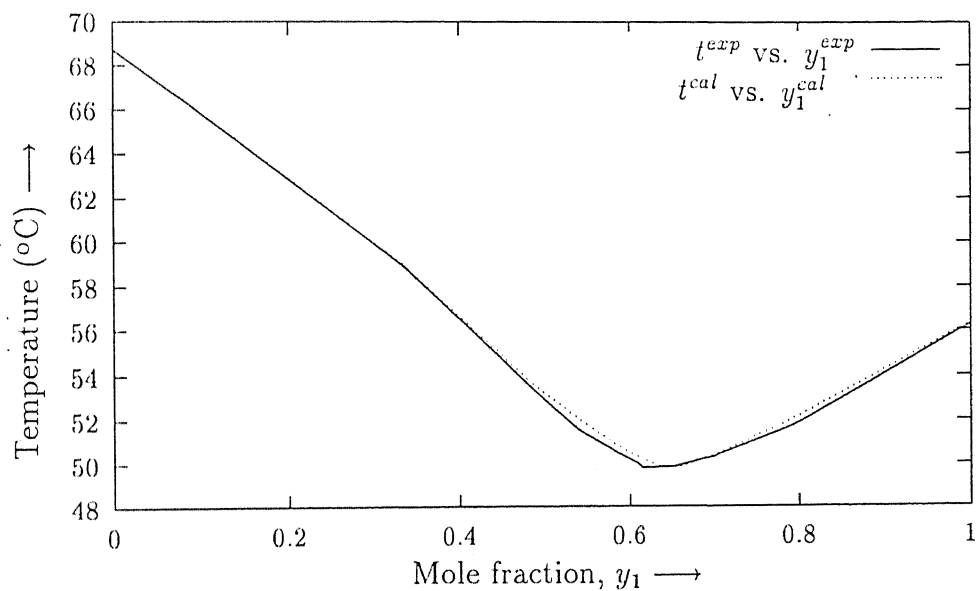


Figure 5.2.3: Comparison of experimental and calculated values of y_i and t from Wong-Sandler mixing rules for Acetone-Hexane at 1.013 bar pressure.

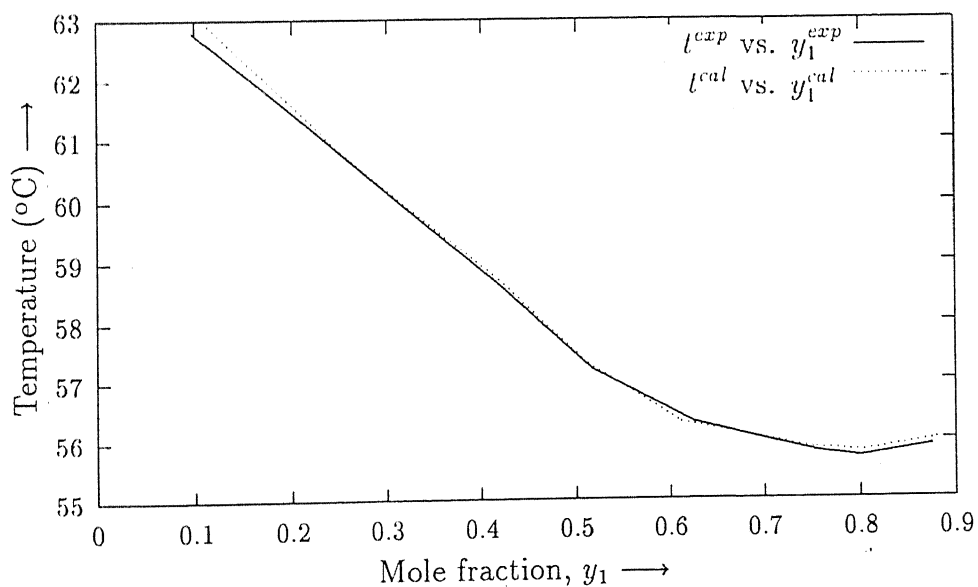


Figure 5.2.4: Comparison of experimental and calculated values of y_i and t from Wong-Sandler mixing rules for Acetone-Methanol at 1.013 bar pressure.

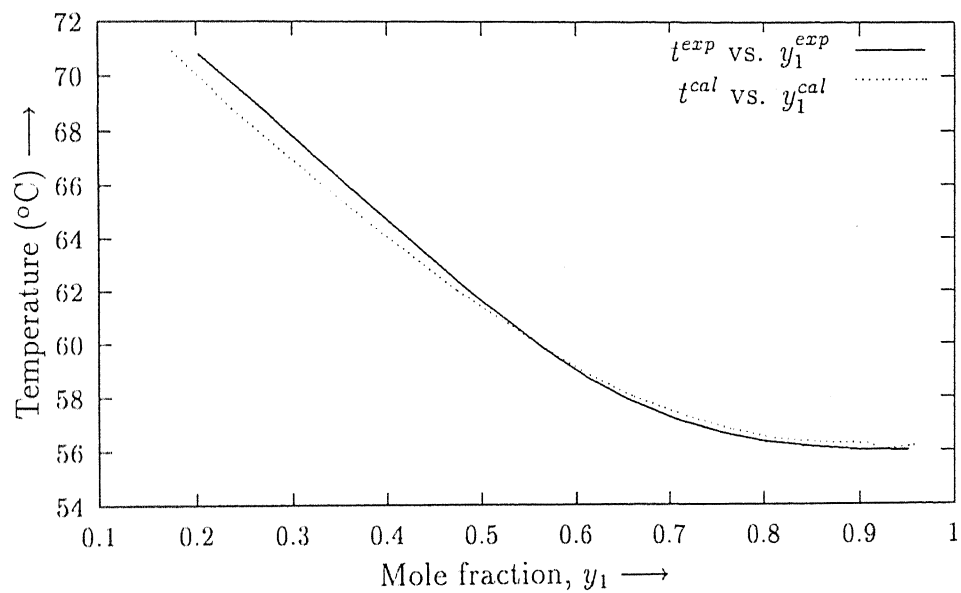


Figure 5.2.5: Comparison of experimental and calculated values of y_i and t from Wong-Sandler mixing rules for *Acetone-Tetrachloromethane* at 1.013 bar pressure.

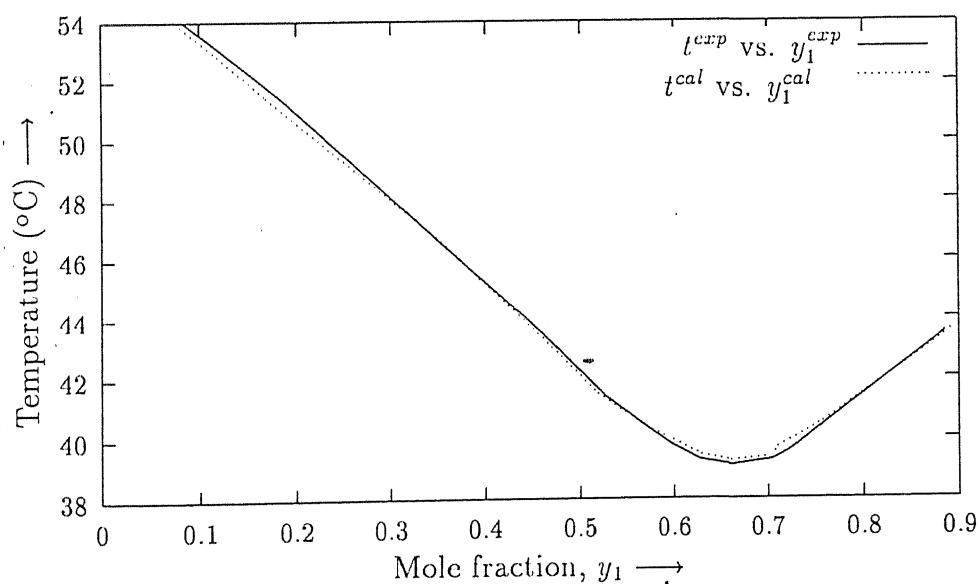


Figure 5.2.6: Comparison of experimental and calculated values of y_i and t from Wong-Sandler mixing rules for *Carbon disulfide-Acetone* at 1.013 bar pressure.

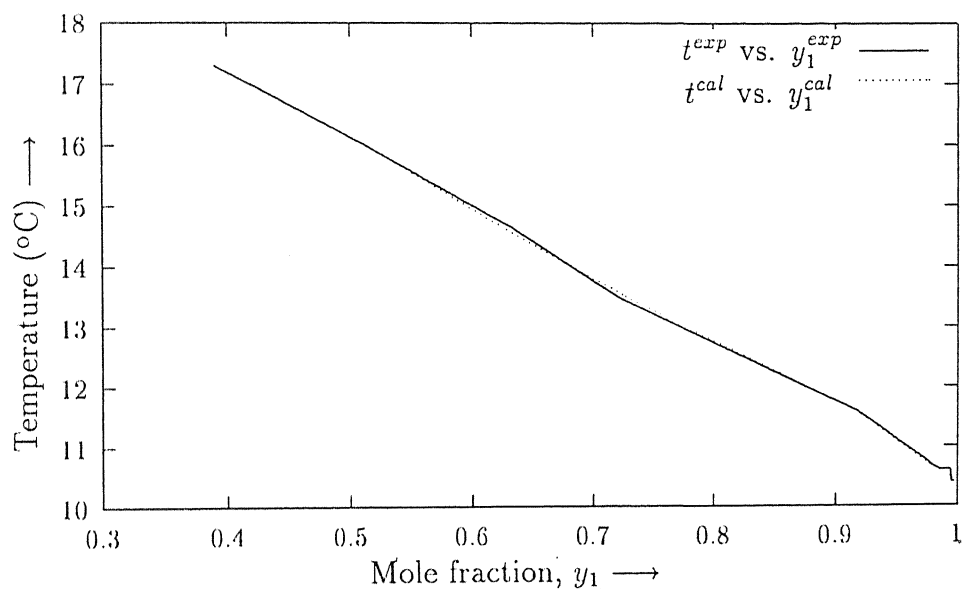


Figure 5.2.7: Comparison of experimental and calculated values of y_i and t from Wong-Sandler mixing rules for *Ethylene oxide-Acetaldehyde* at 1.013 bar pressure.

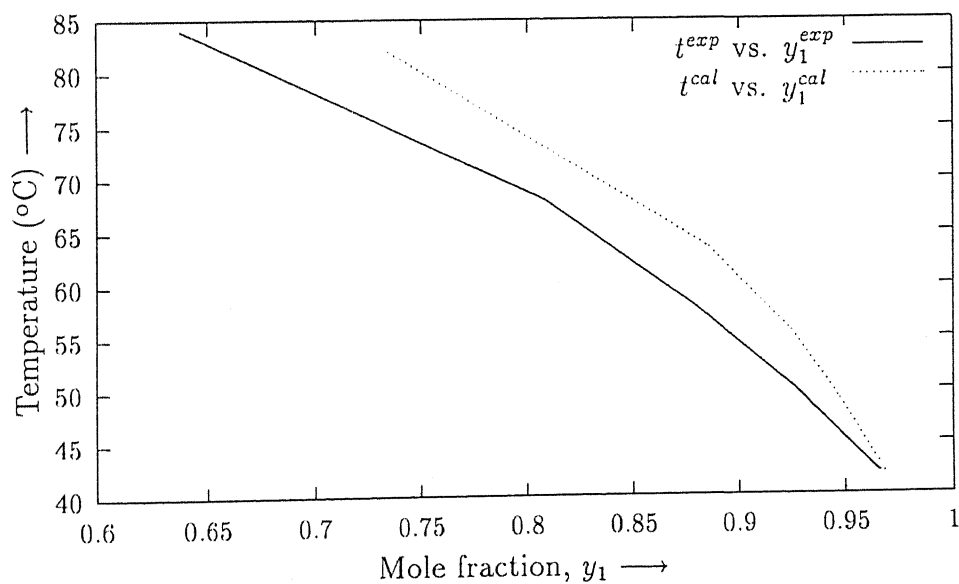


Figure 5.2.8: Comparison of experimental and calculated values of y_i and t from Wong-Sandler mixing rules for *Acetaldehyde-Acetic acid* at 1.024 bar pressure.

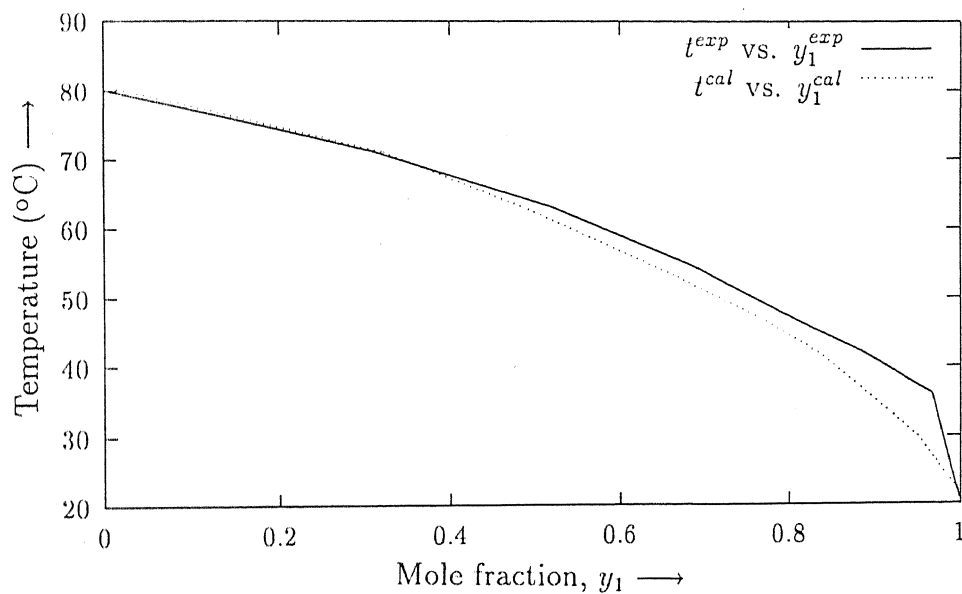


Figure 5.2.9: Comparison of experimental and calculated values of y_i and t from Wong-Sandler mixing rules for *Acetaldehyde-Benzene* at 1.013 bar pressure.

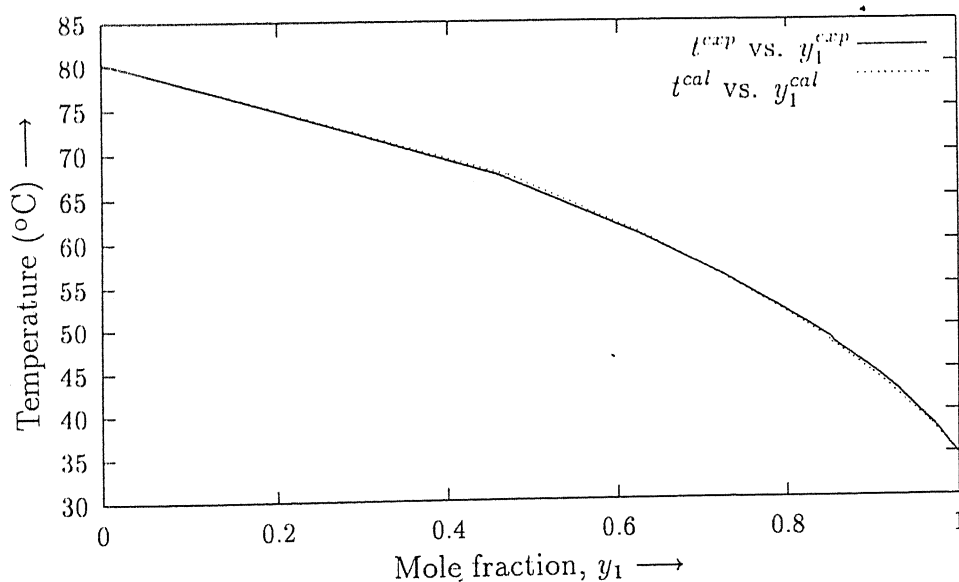


Figure 5.2.10: Comparison of experimental and calculated values of \tilde{y}_i and t from Wong-Sandler mixing rules for *Diethyl ether-Benzene* at 1.016 bar pressure.

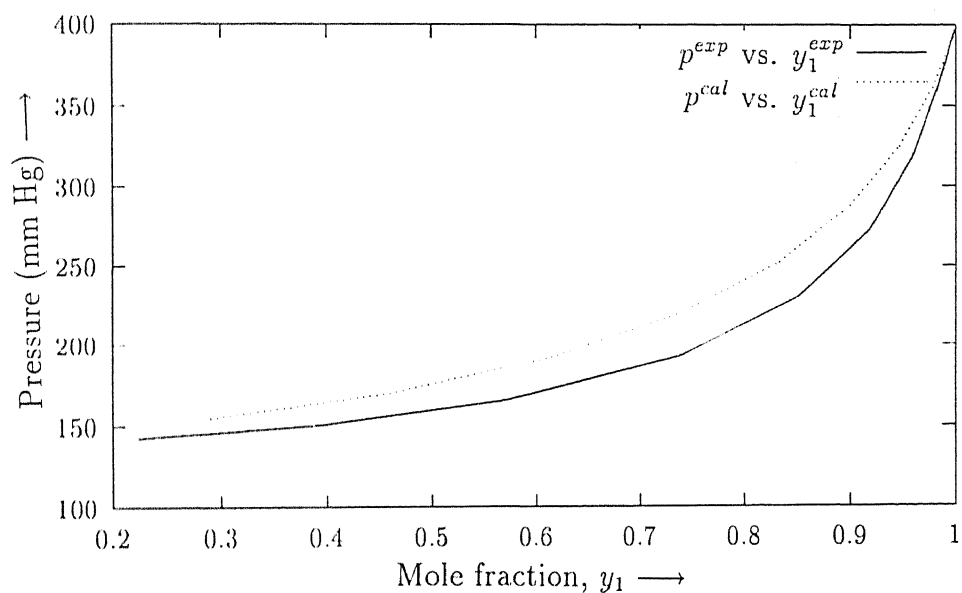


Figure 5.2.11: Comparison of experimental and calculated values of y_i and p from Wong-Sandler mixing rules for *Diethyl ether-Chloroform* at 290.0 K temperature.

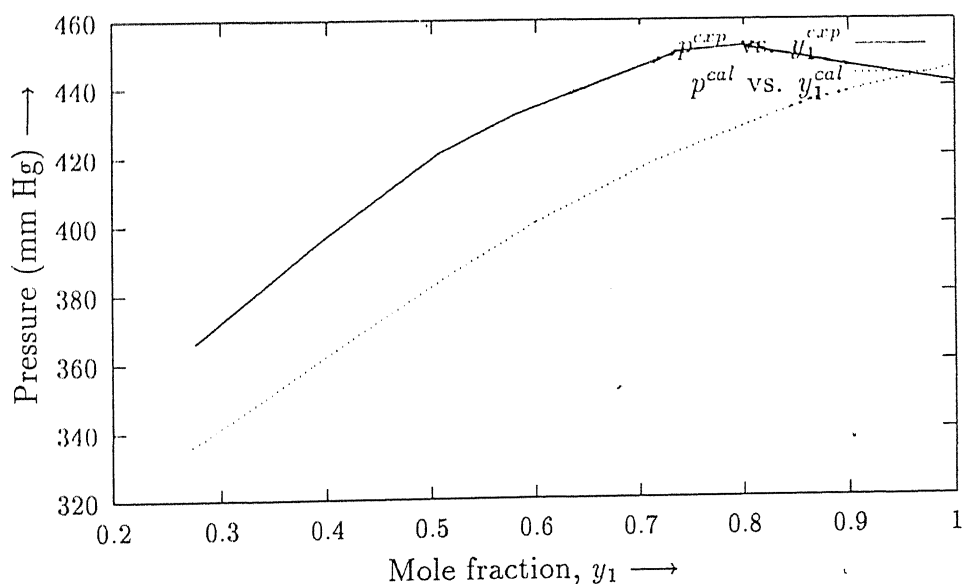


Figure 5.2.12: Comparison of experimental and calculated values of y_i and p from Wong-Sandler mixing rules for *Diethyl ether-Carbon disulfide* at 293.0 K temperature.

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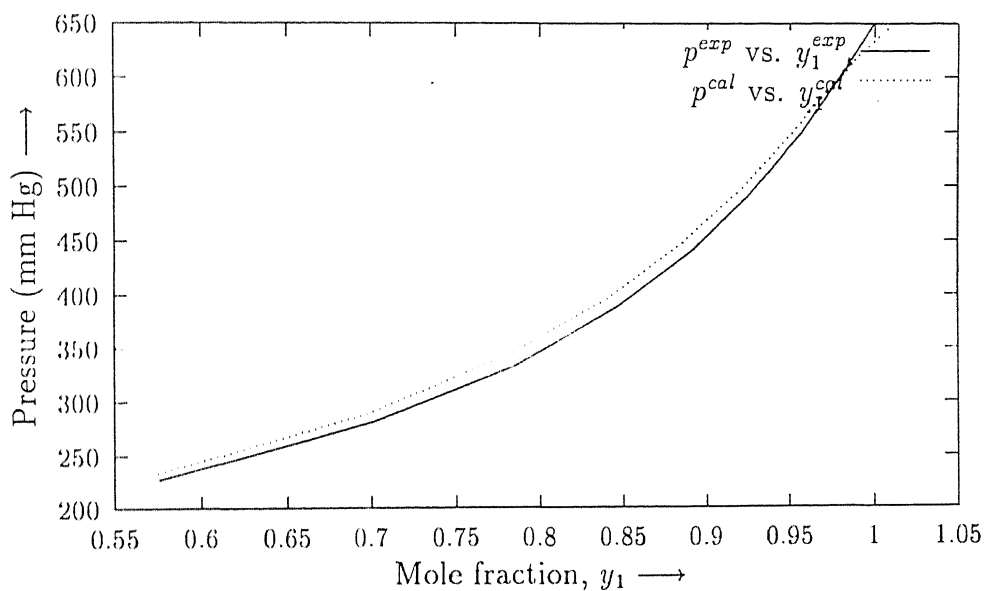


Figure 5.2.13: Comparison of experimental and calculated values of y_i and p from Wong-Sandler mixing rules for *Diethyl ether-Ethyl acetate* at 303.0 K temperature.

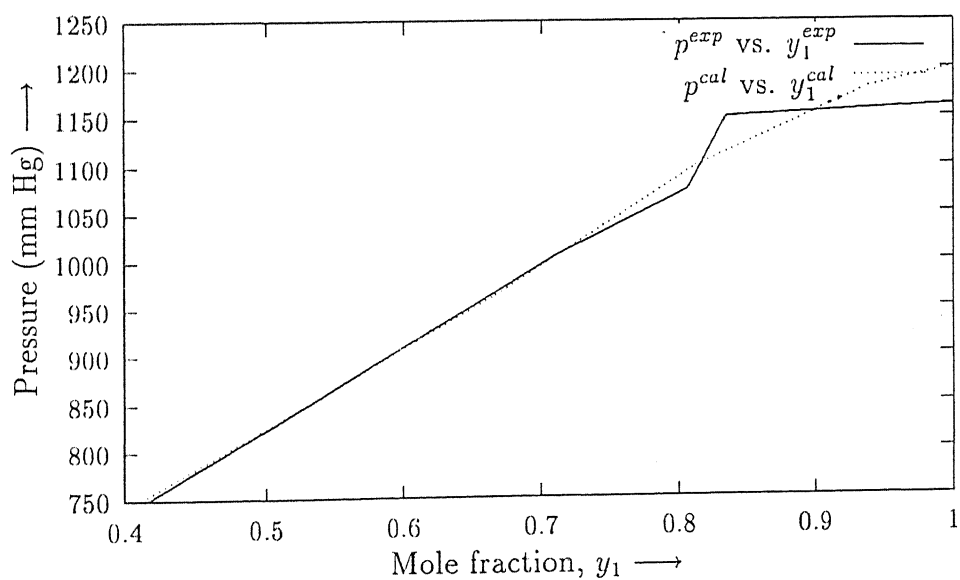


Figure 5.2.14: Comparison of experimental and calculated values of y_i and p from Wong-Sandler mixing rules for *Ethyl chloride-Diethyl ether* at 298.0 K temperature.

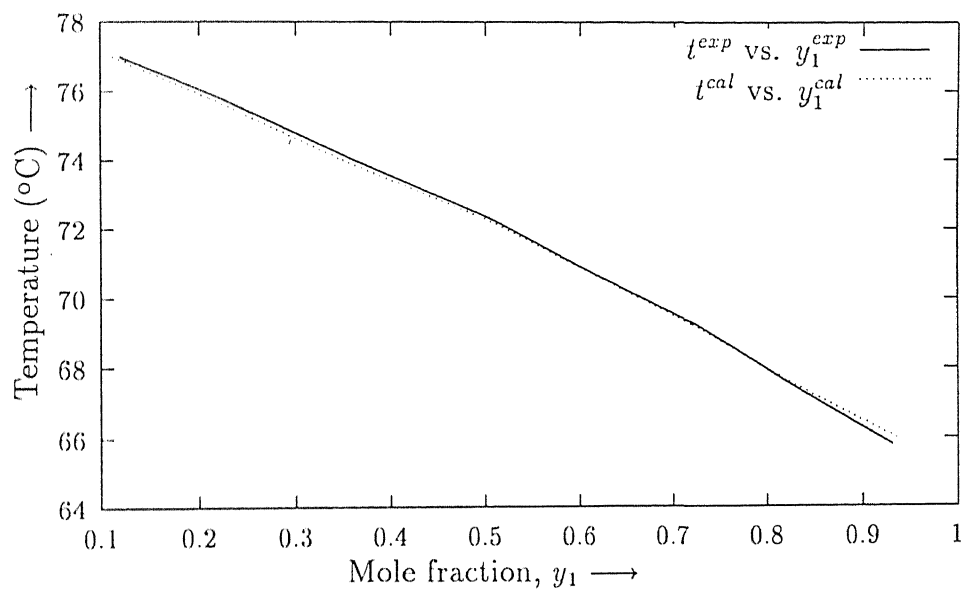


Figure 5.2.15: Comparison of experimental and calculated values of y_i and t from Wong-Sandler mixing rules for *Methanol-Ethanol* at 1.013 bar pressure.

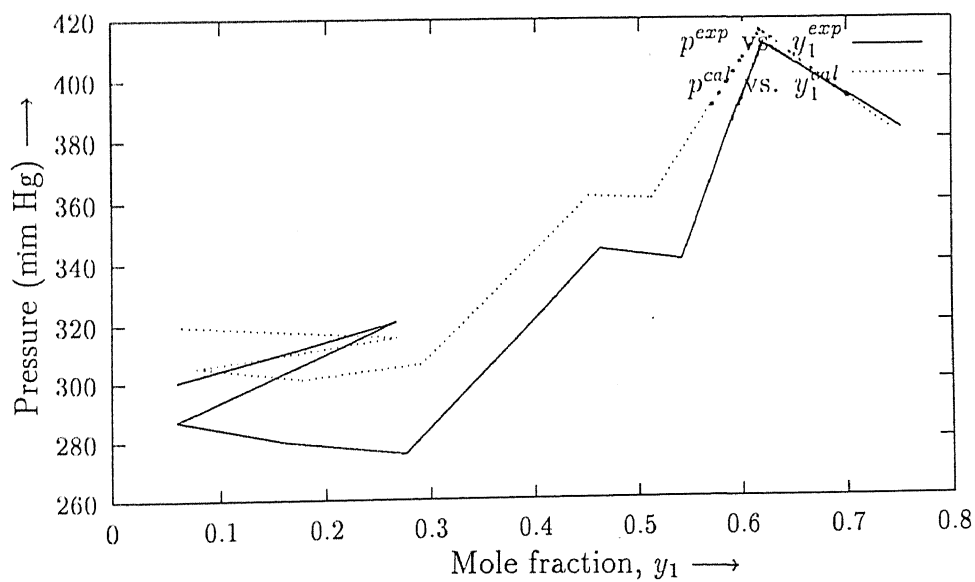


Figure 5.2.16: Comparison of experimental and calculated values of y_i and p from Wong-Sandler mixing rules for *Acetone-Chloroform-Hexane* at 308.0 K temperature.

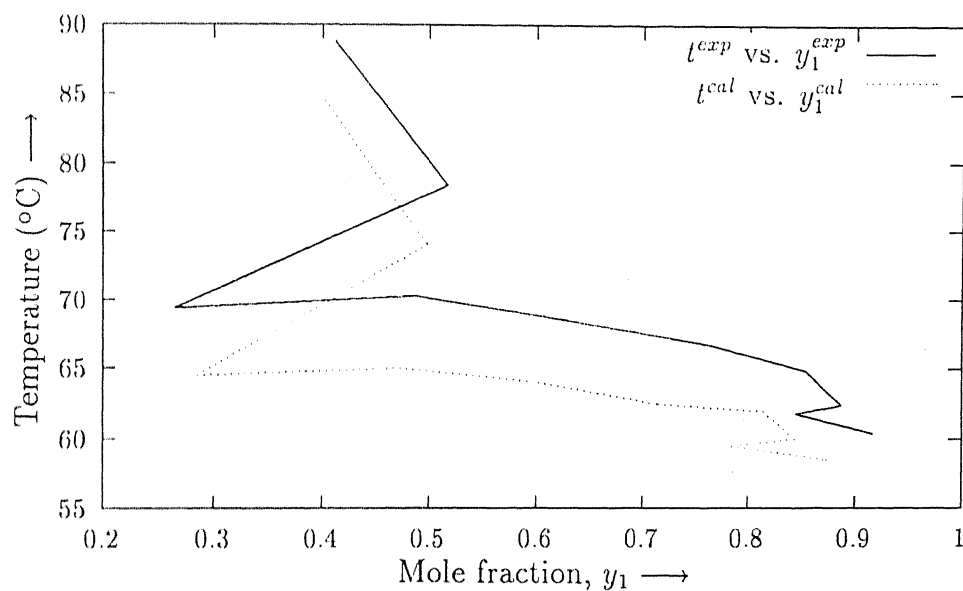


Figure 5.2.17: Comparison of experimental and calculated values of y_i and t from Wong-Sandler mixing rules for *Acetone-Chloroform-Toluene* at 1.013 bar pressure.

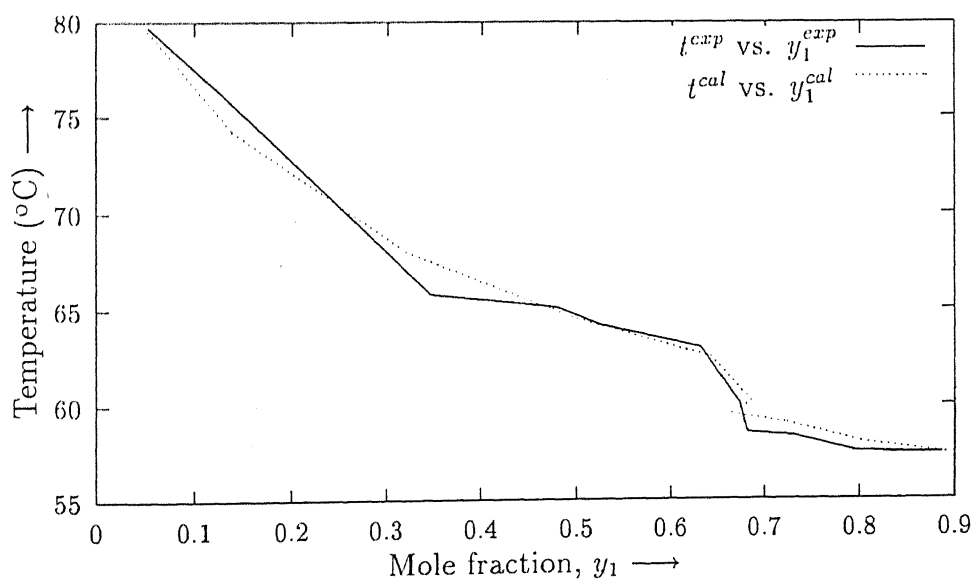


Figure 5.2.18: Comparison of experimental and calculated values of y_i and t from Wong-Sandler mixing rules for *Acetone-Tetrachloromethane-Benzene* at 1.013 bar pressure.

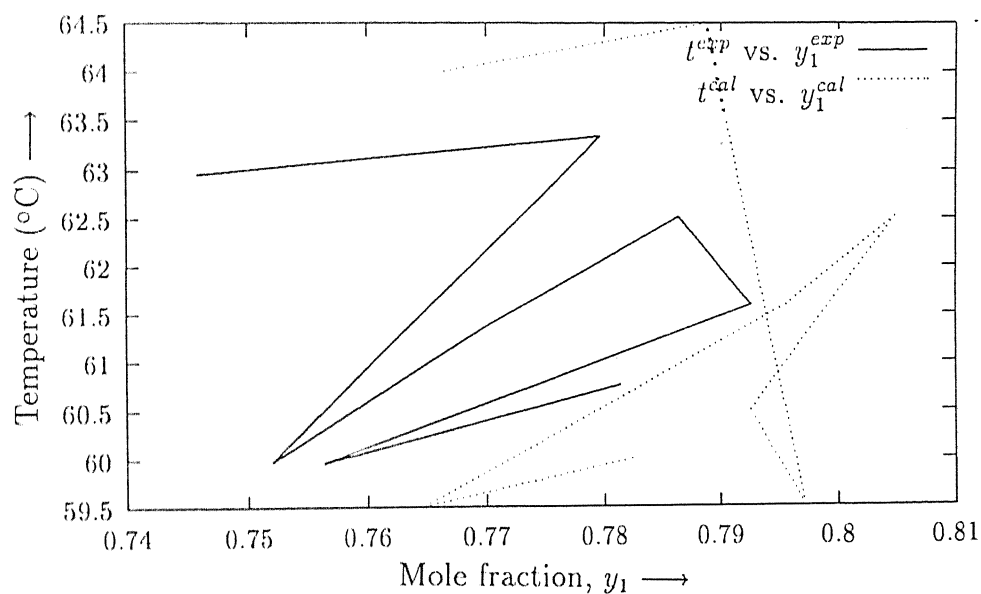


Figure 5.2.19: Comparison of experimental and calculated values of y_i and t from Wong-Sandler mixing rules for *Methanol-Heptane-Toluene* at 1.013 bar pressure.

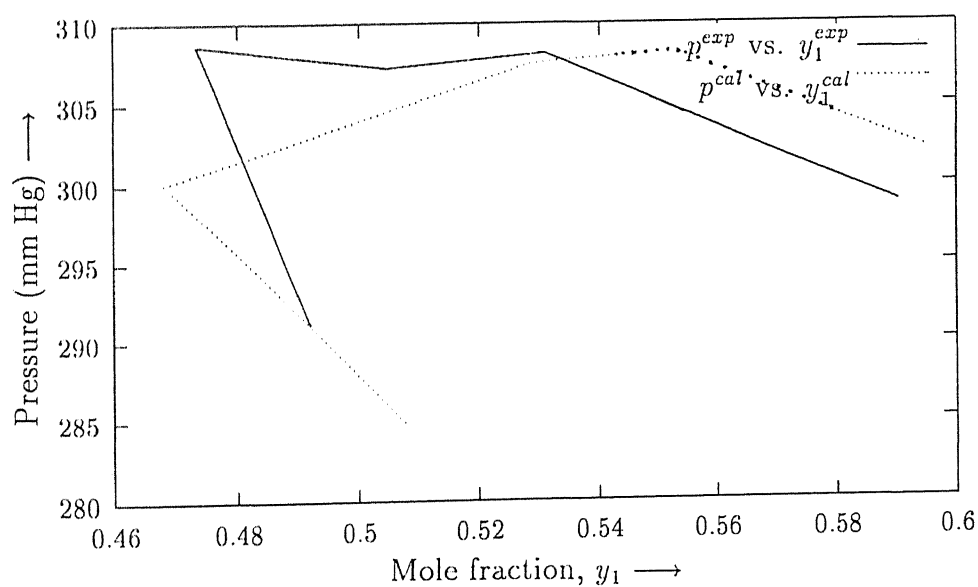


Figure 5.2.20: Comparison of experimental and calculated values of y_i and p from Wong-Sandler mixing rules for *Methanol-Tetrachloromethane-Benzene* at 307.68 K temperature.

Chapter 6

CONCLUSIONS

The equations of state which are applicable to both vapour and liquid phases have obvious advantages over activity coefficient models especially when one is interested in large ranges of temperature and pressure including critical and supercritical regions. However phase equilibrium calculation using equations of state are rather lengthy except for simple equations of state. Another problem with the use of the equations of state technique is the insufficiency of information about the exact form of equations of state for mixtures.

While calculating the cross second virial coefficient by *Tsonopoulos correlation*, binary interaction parameters for cross temperatures have been tuned in order to match calculated results with experimental results. This is one of the disadvantages of this model. But one can overcome this difficulty by using optimization technique (e.g., *genetic algorithm, direct search methods, gradient-based methods*) to determine binary interaction parameters for cross temperatures and these values can be used for other systems at different conditions.

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